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13. ABSTRACT *(Maximum 200 words)*
THE BASIC OBJECTIVE OF THIS STUDY WAS TO RECOMMEND INTERIM PROTOCOLS FOR THE LABORATORY VALIDATION OF SAMPLE COLLECTION, HANDLING AND PRESERVATION METHODS DURING THE INSTALLATION RESTORATION INTERIM GEOHYDROLOGICAL PILOT SOIL/WATER SAMPLING PROGRAM. THE PROTOCOLS WERE INTENDED TO INCORPORATE METHODS OF SAMPLE EXTRACTION, CLEAN UP AND ANALYSIS. THE SCOPE OF WORK ORIGINALLY STATED TO ACHIEVE THE OBJECTIVES OF THIS STUDY WAS DIVIDED INTO 4 GENERAL AREAS AND WAS STATED AS FOLLOWS: 1) REVIEW OF LITERATURE ON ENVIRONMENTAL FATE AND ANALYTICAL TECHNIQUE 2) RECOMMENDED INTERIM VALIDATION PROTOCOLS, 3) VALIDATION OF SAMPLING, HANDLING AND PRESERVATION METHODOLOGY AND 4) EVALUATION OF PILOT FIELD PROCEDURES. THE PROJECT EVOLVED, AS NECESSARY, MEETING THE DEMANDS AND CAPABILITIES OF THE MATERIAL ANALYSIS LABORATORY DIVISION AND THE REQUIREMENTS OF THE INTERIM
GEOHYDROLOGICAL PILOT PROGRAM. THIS PROJECT IS CONSIDERED PHASE II OF PATTERSON ASSOCIATES' INVOLVEMENT AND IS DESIGNED TO SUPPLEMENT PHASE I (METHODS FOR

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METHODOLOGY

FOR

THE VALIDATION OF COLLECTION, HANDLING

AND PRESERVATION

OF

WATER AND SOIL SAMPLES

Rocky Mountain Arsenal

Installation Restoration

May, 1977

PATTERSON ASSOCIATES, INC.

PATTERSON
ASSOCIATES,
Incorporated

ENVIRONMENTAL CONSULTANTS

1540 N. State, 10-D
Chicago, IL 60610
June 17, 1977

Mr. Irwin Glassman,
Director
Installation Restoration
Rocky Mountain Arsenal
Denver, Colorado 80240

Dear Mr. Glassman:

In accordance with the agreement between Rocky Mountain Arsenal and Patterson Associates, Inc., we transmit herewith our final report on Methodology for the Validation of Collection, Handling and Preservation of Water and Soil Samples. As you are aware, this report has been delayed sixty days beyond the original date of submittal in order to provide maximum opportunity for interaction between MALD and our staff, thus allowing the report to incorporate final recommendations based upon the most recent results of MALD in assessing methodologies of concern in the IR Interim Geohydrological Pilot Program.

In preparation for this project and during its course, five joint meetings were held between representatives of RMA and Patterson Associates, for project planning and coordination. In addition, there was one meeting held with the Analytical Systems Committee (3 March 1977). These meetings are listed below:

Date	Location	Represented
12 December 1976	Chicago	IR-MALD, PAI
19-20 February 1977	RMA	Edgewood, IR, PAI
2-3 March 1977	RMA	Edgewood, IR, PAI
3 March 1977	RMA	ASC, PAI
29 April 1977	RMA	Edgewood, IR, PAI
27 May 1977	Chicago	Edgewood, IR-MALD, PAI

These meetings were invaluable in allowing proper planning and liaison in support of the project goals.

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The project has been dynamic in nature, evolving as necessary to meet the demands and capabilities of the Material Analysis Laboratory Division, and the requirements of the Interim Geohydrological Pilot Program. As a result of this evolution, various recommendations submitted during the project were modified at the discretion of MALD, and the results of those modified procedures are incorporated into and discussed in this report.

Sections III.C and IV.B of this report contain our final recommendations, based upon our experience with and assessment of MALD efforts since project initiation. These recommendations are presented and discussed in the cited report sections. However, I wish to particularly call your attention to Recommendation No. 3, page 31. As documented in the report, it is our recommendation that until such time as adequate methodology has been developed under the auspices of the Analytical Systems Committee, or developed by MALD with the concurrence of ASC, soil analyses for DCPD should not be conducted. Further (see page 32), due to uncertainties associated with soil core storage, we strongly urge that all soil samples be immediately extracted. As noted in our report this requires that the rate of drilling be closely coordinated with MALD extraction activities.

Cordially yours,

James W. Patterson, Ph.D.

JWP:mk
Encl.

METHODOLOGY FOR THE VALIDATION OF COLLECTION, HANDLING AND PRESERVATION OF WATER AND SOIL SAMPLES

Rocky Mountain Installation Restoration

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I. INTRODUCTION

Water Management

A. During FY77 the DECON TECH, Task of the IR program focused on development of a pilot system to contain and treat contaminated ground waters crossing the north boundary of Rocky Mountain Arsenal. The final design for this pilot has been developed and the system should become operational in mid-FY78. The data from this pilot will be used to develop a final treatment system. Program emphasis in late FY77 turned to development of mechanisms to eliminate or contain the pollution sources at RMA. This work will increase in FY78. The boundary work is not being discontinued but rather it is being complimented by the pollution source control work. Without control of pollution sources, the boundary system would have to operate for an extended period of time.

B. During FY78 the DECON TECH program will be operating on two broad fronts: first, the development of processes to control the pollution sources; and second, the implementation of test systems to contain and treat contaminants in the ground waters of RMA. In the beginning of FY78 the process development work will be the largest effort. Toward the end of the fiscal year, however, a large program effort will develop in systems implementation.

C. Process Development. The various efforts within process system development have been divided into discrete but interrelated research areas. These areas are:

- Water Treatment technology (includes surface and ground water treatmen
- Process wastes and sludge treatment.
- Soil treatment.

(1) The water treatment process development research area is the most advanced of all the areas at this time. Through the studies conducted in this area, processes are being developed to remove contaminants from surface and ground waters. The developemnt of the granular carbon process for the north boundary pilot system was a part of this work. Studies are now being oriented to develop a process system for the more concentrated amounts of contaminants found in the ground water at and near the pollution sources. Establishment and operation of a ground-water treatment system at the pollution source in conjunction with a pollution source control mechanism (treatment/contaminant) would reduce the time of operation for the boundary contaminant system.

(2) Studies in process waste and sludge treatment will be emphasized in the FY78 program. These studies will be oriented toward treatment and ultimate disposal or reuse of the water treatment process side stream wastes and sludges. Some work has been accomplished in this area with the conduct of the granular carbon regeneration study done by Calgon Corporation, and the powdered carbon disposal/regeneration study by the Chemical Systems Laboratory. The FY78 program will pursue the investigation of the fate of pollutants absorbed onto the carbon during regeneration and will also look into methods of disposal for sludges derived from other developing processes (i.e., inorganic treatment processes).

(3) Soil treatment studies will be initiated in FY78. These studies will investigate both insitu and excavated methods of treating contaminated soil. From this research the methods and systems for treatment of the pollution sources will be developed.

(4) Process systems developed for the RMA program will have a broader application than just one installation. The process concepts will be developed with an eye toward broad application. As other IR program treatment requirements are identified, these methods can be reviewed and, if applicable, implemented with a much reduced developmental effort.

D. Process Implementation. The implementation phase of the developed processes started during FY77 with the design of the RMA north boundary pilot contaminant and treatment system. Process implementation includes establishment of the pilot, as well as the testing associated with pilot expansion, and is broken down into the following work areas:

- Water management and contaminant systems analysis (includes both ground and surface water).
- Treatment process system analysis (includes both pilot and final process implementation and orientation).

(1) The water management and contaminant studies are oriented toward investigation of measures that can be taken to prevent a specific pollution source from contaminating ground or surface water. This area of work also includes investigation of mechanisms by which water can be withdrawn and resupplied to the water system without detremental effects on water supplies of downstream users. Some work in this area was done in preparation of the design for the north boundary pilot systems. Some preliminary work has also been done on evaluating methods to totally contain the pollution sources,

preventing further contamination migration from these sources. During FY78 this work will be expanded and methods for pollution source containment will be further investigated as will the available methods to flush for treatment the already contaminated ground water moving toward the RMA boundary.

2. The treatment process implementation work will commence in FY78 with the installation of the process for the north boundary pilot system. This work will commence in the first quarter of FY78. Additional work is anticpated in this area toward the end of FY78 when combinations of unit processes will be tested to determine the best process for the final north boundary system.

3. Programs and Schedules.

a. Water treatment technology development.

(1) During FY78 water treatment will be pursued for removal of both organic and inorganic contaminants. The organic removal processes are at a more advanced stage of development than the inorganic due to the work completed in FY77. The processes being studied are granular carbon adsorption and ultraviolet light ozone.

(a) Ultraviolet light ozone.

● Planned Work

The ultraviolet light ozone work will be pursued on a bench scale as well as a field scale (1-5 gpm) level. The bench work will be oriented toward determining the best reactor design for treatment of contaminated ground water across the Arsenal. Water samples from the north boundary, well 118 (Basin F area), and well 11 (Basin F area) will be processed. The results of these studies will be compared to the field scale test results; initially the field scale tests will be done on a reactor leased from Ultrox Corp in

California. The initial tests will be used to determine and verify scale-up requirements for the process. Once this testing is complete, a modified desig reactor will be procured. The design of this unit will be based on the results of the bench scale work and will be able to accommodate the varing quality of ground water requiring treatment. This work was started in the last quarter of FY77 and will continue through FY78. A schedule of planned UV-O_3 work is shown at Figure 1. The FY78 work will initially be oriented toward treatment of ground waters north of Basin F (north boundary to well 11! These results will be reviewed with respect to implementation of a final nort! boundary treatment system. The testing will continue and move into treatment of water south of Basin F into the Basin A area (well 11). Time has been allowed in the schedule shown to evaluate treatment of ground water at sources other than Basins A and F should additional sources be discovered. The combined results of these studies will provide information from which a I O_3 process could be designed to remove organic contaminants from ground wate: at the sources of any point along the contaminant migration route. The UV-O, testing should be complete in FY79 for all sources.

Checkpoints:

The UV-O_3 work will be continually evaluated for applicability and cost effectiveness. Certain specific key checkpoints for program have been identified; however, at these checkpoints the completed results for that po: of the testing program will be reviewed and a decision will be made as to tl continuation of testing. The identified points are at the end of FY77 test: and at the completion of north boundary and well no. 118 testing. At the e: FY77 testing, the evaluation of the efficiency of the leased unit, as well some insight into scale-up requirements, should be known. If the test results at this time show that the process is not cost effective or that the process is not applicable to the given problem, the test program will be discontinued. At the completion of testing on the north boundary and Basin F area samples, the test results will again be reviewed. These results should show specific process requirements for removal of organic contaminants in the area north of Basin F to the north boundary. Again, cost effectiveness and treatment applicability will be evaluated with respect to continuation of the program.

(b) The granular carbon bench and field study work for the north boundary were completed in FY77. Based on this information, the design for a treatment process in conjunction with the north boundary pilot has been developed. This process will be constructed during the first quarter of FY78.

(2) The inorganic treatability studies were initiated in late FY77 and will continue in FY78. These studies will be pursued at the bench scale and field scale during FY78. The initial bench work will be oriented toward treatment of ground water in the Basin F to north boundary area. As these tests are completed, testing will begin in the Basin A and other identified pollution source areas. After sufficient data has been gathered on the bench level, field testing of the processes will start. This testing is currently targeted for initiation in January of 1978. By the end of the third quarter of FY78 sufficient process information should be available for the north boundary to Basin F area. This information will be coordinated with the organic process data to develop a finalized treatment scheme on the north boundary system. Field studies with the inorganic processes will continue on the Basin A area and other identified pollution sources into FY79. After completion of these studies, all process information will be reviewed and a ground-water source processing system developed.

The same type of decision points are planned for these inorganic studies a for the organic treatability studies. The program will be checked for cost effectiveness and applicability at the initiation of field studies, and after the results of the well 118 to the north boundary portion of the study are complete. The results of the north boundary pilot monitoring will also be compared to the proposed and existing standards for inorganics if the operation of the system sufficiently averages the concentration of these contaminants and reduces them below the required levels, the treatment development effort for inorganics will be reduced. The effort could not be toally terminated because of the requirements for treatment in the source areas.

B. Implementation of Developed Water Treatment Processes.

1. Granular Carbon .

a. As noted before, the developmental work on the granular carbon process is complete. A carbon adsorption process will be installed as part of the nort boundary pilot system. This construction will be constructed during the first quarter of FY78 and used to treat construction waste waters from the dewatering and recharge well testing during the second quarter of FY78. The total system will become operational in mid-FY78. The data from this operating pilot will be monitored to assist in development of a final north boundary treatment complex. The operating facility will also provide information on the flow of ground water to the system and the resultant average concentration of contaminants requiring treatment. There is a possibility that if conditions are favorable the north boundary system will have minimum expansion requirements. These conditions will be watched closely to insure that only the required expansion is done.

2. Combination Process Testing.

a. After completion of developmental work for the organic and inorganic treatment processes for the north boundary area of RMA (Basin F to the north boundary), the processes will be tested in combinations to determine the most effective systemization. These tests will start in the last quarter of FY78 and be completed by the end of the first quarter FY79. After completion of these tests, design criteria will be developed for the expanded treatment system for north boundary contaminant migration control. The decision as to what processes will be tested in combination will be based upon the results of the lab and field studies and the treatment requirements identified by monitoring the influent water quality of the operating pilot system. Only the required treatment process will be tested for integration into the final system design criteria development.

b. A similar type combination process study will be conducted at the completion of the source treatment process studies. These studies are currently targeted to start in the fourth quarter FY79. If no sources other than Basins F and A are found, these studies might start sooner in FY79. These studies should be completed with design criteria developed at least by the end of FY80. Again, the field testing results will be closely monitored and only the applicable processes will be integrated into the final system combination tests.

3. Design Procurement and Construction.

It is estimated that design, procurement, and construction will take approximately 12-15 months after design criteria is complete. Based on this timing, the final north boundary system would be complete and operating during FY80 and pollution source water processign could be operative in FY82. Again, if no additional pollution sources (other than Basins F and A) are discovered, this system might be operational in FY81. The operation of these systems could be done in conjunction with source soil treatment or source containment.

4. Water Treatment Process Waste Side Stream and Sludge Studies.

a. In conjunction with the development of the water treatment processes, waste process systems will also be developed. These waste processes are needed so that as a sludge on side stream waste is delivered from a treatment unit, it can be processed for reuse or ultimate disposal. To date some work has been done in this area; namely, the powdered carbon regeneration testing from the Calgon granular carbon system. This work, however, was short term. In the case of the granular carbon only regeneratic furnace emission testing was done to determine if any compounds were present that would preclude use of the regeneration process. The comments on the Draft EIS for this process stressed the need to know how the adsorbed compounds interacted and what their fate was as a result of regeneration. T type of information will be developed by this study area.

b. During FY78 the regeneration of granular carbon will be studied in more detail as will disposal/regeneration systems for the inorganic treatmen processes. In line with the schedule (Figure 2) a review of all processes under study will be made and the type wastes expected from the processes wil defined. From this evaluation a study plan will be prepared and forwarded t the Office of the PM CDIR for review prior to commencement of work. The actual conduct of the work will be split into two phases as is the treatment process development work. The initial effort will be oriented toward development of disposal/reuse processes for the wastes developed by the

North Boundary treatment processes. This work will include the granular carbon regeneration study. This work will be conducted on a laboratory and field study scale as it is applicable for the processes under review. The second phase of this work will be oriented toward disposal/reuse of waste products delivered by the pollution source treatment unit. The results of both phases of this study will be coordinated with the combination water treatment process testing discussed in para _____ above.

C. The schedule for completion of this disposal/reuse process development work is largely dependent upon water treatment process development. It is estimated, however, that laboratory work on disposal/reuse processes will be complete by the end of FY78 and field studies will be completed by 4QFY79. The results of all these studies will be used in the combination process testing and design criteria development for a final treatment system.

5. Soil Treatment Studies.

a. The primary cause of ground-water pollution at RMA is the leaching of contaminants from waste disposal areas into the ground-water system. These waste disposal areas are referred to as the pollution sources. The leaching from these sources may be from a point source of disposed waste, but more likely it is believed that the long term and continuing source is from the leaching of soils heavily ladden with contaminants. These contaminated soils must therefore be evaluated and treated if the migration of this pollution is to be stopped.

b. The development of soil treatment processes will be pursued on two fronts: namely, insitu and excavated soil treatment work. The insitu work will investigate processes such as chemical fixation, vegetative uptake, and bio-transformation of contaminants. The excavated soil treatment work will investigate processes such as thermal and chemical neutralization. The Basin F source area is largely a unique liquids and sludge problem that will be handled under a separate area (this area will be discussed later).

c. Starting in the 1QFY78, an evaluation of all pollution source soils dat will be made. It is expected that the bulk of this data will be from the Basin A area and derived from the ongoing pilot comprehensive survey work. Als information will be available on the ground water quality in the area. This data will come from the comprehensive survey work as well as the ongoing pollution source and water treatment study being done by the Chemical Systems Laboratory at Aberdeen Proving Ground, MD. After review of these data, a study plan will be developed for both insitu and excavated soil treatment. The study plan will provide for as quantitative a review as is possible of applicable treatment schemes. It is recognized that it is not cost effective nor affordable to develop all or possibly even many methods of soil detoxification. Therefore, the 1st quarter evaluation should include a qualitative assessment of all potential processes and only the most promising technologies should be quantitatively evaluated during the remainder of the fiscal year. Heavy consideration should be given to cost effectiveness and process applicability when the selection of processes for quantitative study is made. The results of this FY77 work should show the costs of the various processes, both for such development and implementation, as well as the advantages and disadvantages of each process. Based on this work, the FY79 and FY80 process work can be finally determined and developed. These studies should be complete with the development of final system design criteria by the end of FY80.

6. Containment Systems Evaluation.

a. The development of treatment processes will progress rapidly in FY78 and by the end of the year, a good synopsis of complete treatment requirements, developmental and implementation costs, and operating costs will be available. These treatment requirements, costs, and time estimates will be compared to the requirements, costs, and times for total containment of the pollution sources. The containment data will be developed under this portion of the decontamination technology program.

b. During FY77 Basin F and Basin A qualitative containment studies were completed. These studies identify specific areas of work for quantitative evaluation and design criteria development for the containment types specified. In FY78 these quantitative studies will be pursued. At the end of these studies, quantitative data as to design, procurement, and construction costs and times will be available. This information will be compared to the treatment information and a decision will be made as to the types of containment and/or treatment schemes to be employed. Of course, if treatment is chosen over containment, the planned treatment work schedules discussed previously will be employed. If, however, the treatment effort is reduced or eliminated, the work schedules and costs for treatment works be altered accordingly. The work schedule for containment implementation in FY79 is dependent upon the results of the FY78 studies. It is presently estimated, however, that if containment is employed at any level, it could be completely installed by the end of FY79.

c. In the first quarter of FY78, a study plan for conduct of the quantitative studies will be developed. This plan will be reviewed by the Office of the PM CDIR prior to commencement of the studies. The studies themselves should be complete and design criteria developed for the type(s) of containment system(s) recommended for implementation. Any treatment requirements for the containment systems presented should be identified. Cost effectiveness and applicability of a system to the given field conditions at RMA should be evaluated and only the most feasible system(s) should have design criteria developed. If containment is found to be infeasible, the reasons why should be stated. After design criteria is developed, a recommended approach to FY79 design, procurement, and implementation should be presented.

7. Water Management Studies.

a. The water management studies involve study of the water systems and th methods by which water can be pumped and/or piped in conjunction with a containment and/or treatment system such that the original water conditions are maintained and minimal water loss occurs. Some work of this nature has been done in conjunction with the north boundary pilot system. In order to expand this system, however, and in order to support some of the insitu soil treatment studies, additional work will have to be done in this study area. work would be done primarily between the north boundary and Basin F, in the Basin F area, and in the Basin A area.

b. In the 1st quarter of FY78 the available geo-tech data and ground-wat data on the areas of concern would be evaluated and from this evaluation a st plan should be oriented toward developing quantitative data as to the quantit of flows and aquifed characteristics in the study areas selected. Also, the plan should include provisions for field testing of various pumping and recharge well arrays on a small scale. This plan would be forwarded to the Office of the PM CDIR for approval prior to implementation. The data gained the field testing should be such that quantitative estimates of water managem systems requirements and costs can be made for the north boundary system expansion and for source water treatment/containment systems. The total term of these tests is dependent upon the schedule of treatment development and requirements. It is estimated however that these type tests will continu through FY79.

BASIN F

a. The treatment and elimination of Basin F is being worked on as a separate study area. The above listed study areas could be applied in whole or part to installations other than RMA but the Basin F problem is unique to R

b. The treatment of Basin F is being approached in four phases. These are:

Phase I - Problem Definition

Phase II - Basin Characterization and Pretreatment development

Phase III - Treatment System Development

Phase IV - Construction of Treatment System.

Also, the containment studies discussed in para ___ will run concurrent with Phases II and III.

c. Phase I was initiated in FY77 and will be complete with a final report written by October 1977. This report will include a comprehensive history of the Basin and also the analytical results of samples taken across the basin. The samples were not only taken at the surface but also through the depth of the basin and include samples of the basin's bottom sludge. The results of the Phase I work will define the requirements of Phase II and III actions. Based on the sampling results of Phase I, it is hoped that only minimal additional characterization work will have to be done in Phase II and that pre-treatment work can be emphasized. Pre-treatment testing is scheduled to start in the beginning of FY78. From the pre-treatment work, the Phase II treatment studies will be quickly picked up. It is estimated that these studies ~~will commence~~ in mid-FY78 and are targeted for completion by the end of FY79. These studies will form the base from which a final treatment system is designed, procured, and constructed. This implementation work is estimated at 15-18 months and treatment would begin in FY81.

d. Concurrent with Phase II treatment studies, a commercial industrial survey will be conducted. This survey will be oriented toward determining if a commercial firm is interested in processing Basin F for recovery of metals or other compounds. Also, commercial disposal contracts will be evacuated. Th results of this survey will be used to determine if it is more cost effective for the Government to go commercial contract for disposal of the basin rather than developing a treatment scheme.

e. Basin F containment studies will also be conducted during FY78. These types of studies are discussed in para ____. At the end of FY the estimated tre ment requirements, costs, and timing will be compared to the containment study results, and a decision will be made as to the containment and/or treatment approach to be pursued.

✓ 9. Funding.

The funding for the RMA R&D program discussed above is shown in Table 1. This funding distribution assumes full funding in FY78. If FY78 funding is cut, some of the above described work will have to be decreased in scope or eliminated. The exact reduction of work cannot be determined until the amount of the budget cut is known.

TABLE 1

		FY78	FY79	FY80
1.	Water Treatment Studies (Including Design Criterial Development)	450K	375K	350K
2.	Treatment Process Waste and Sludge Studies	200K	175K	0
3.	Soil Treatment Studies	300K	400K	400K
4.	Containment Studies (Basins A and F)	400K	0	0
5.	Water Management Studies	210K	200K	100K
6.	Basin F Study	400K	350K	0

METHODOLOGY FOR THE VALIDATION OF COLLECTION, HANDLING AND PRESERVATION OF WATER AND SOIL SAMPLES

Rocky Mountain Arsenal Installation Restoration

I. General

A. Background

The basic objective of this study was to recommend interim protocols for the laboratory validation of sample collection, handling and preservation methods during the Installation Restoration Interim Geohydrological Pilot Soil/Water Sampling Program. The protocols were intended to incorporate methods of sample extraction, clean up and analysis. Statistical evaluation methods were to be proposed to ascertain the impact on precision and accuracy of sample collection, handling and preservation procedures. These results when incorporated with the existing quality control program developed by the RMA-MALD personnel concerning extraction and analysis were to provide overall precision and accuracy limits for the I R Interim Geohydrological Pilot Program.

The project, considered Phase II of Patterson Associates', Inc. involvement with the Rocky Mountain Arsenal Installation Restoration Program was designed to supplement Phase I (Methods for Collection, Handling, Preservation and Storage of Water and Soil Samples, Final Report April 1977, Patterson Associates, Inc.) and coincide with the preliminary development of the pilot field studies to allow meaningful data acquisition during the pilot studies.

B. Scope of Work

The scope of work originally stated to achieve the objectives of this study was divided into four (4) general areas and was stated as follows:

1. Review of Literature on Environmental Fate and Analytical Technique

A critical review of pertinent information on environmental fate and analysis will be conducted. The review will consider information on the potential loss of material from core soil and interstitial water samples by volatilization, adsorption, hydrolysis, biodegradation and other mechanisms. The main objective of the literature review will be to review procedures for handling core and water samples and for contaminant extraction. Alternative methods of chemical analysis will be suggested where appropriate, to validate sample collection and preservation procedures. Literature references and copies of key articles will be provided.

2. Recommended Interim Validation Protocols

In order to expedite the validation of the sampling, handling and preservation techniques employed in the Pilot Soil/Water Sampling Program, protocols for analysis of core soil and interstitial water samples will be recommended. These protocols will incorporate consideration of potential analytical interferences and degradation of materials. The extent of protocols to be provided will correspond to the anticipated "high priority" contaminants requiring analysis during the Pilot Program, as listed below:

DCPD
DIMP
Aldrin
Dieldrin
Endrin
Arsenic Compounds

Mercury and Mercury Salts
p-Chlorophenyl methyl Sulfide
p-Chlorophenyl methyl Sulfoxide
p-Chlorophenyl methyl Sulfone

In the event that analytical techniques are developed by the Analytical Systems Committee in conjunction with the RMA MALD personnel on the additional contaminants tabulated below, further protocols will be provided where possible within the time frame and budgetary constraints of the proposed project.

Nemagon
Tetrachloroethylene
Hexachloronobornadiene
Hexachlorobutadiene
1, 4 - Dithiane
Tetrachlorobenzene
1, 4 - Thioxane
Isodrin
Trichloroethylene

Contact will be maintained with RMA MALD personnel to assure the ability to utilize these protocols by virtue of availability of MALD facilities, equipment and personnel. Procedures for extraction, separation, concentration and analysis operations will be referenced. By isolating these operations, both individual component and overall accuracies can be established. In order to incorporate boundaries on precision and accuracy of analytical methodologies into the validation protocols, internal MALD procedures and analytical results will be reviewed in cooperation with MALD personnel.

3. Validation of Sampling, Handling and Preservation Methodology.

Following the determination of valid analytical procedures, it will be possible to validate the sampling, handling and preservation methodology. This will be accomplished concurrent with the Pilot Soil/

Water Sampling Program. Procedures to determine the extent of sample contamination or loss of constituents associated with field operations will be proposed. Protocols to determine influence of storage time and storage conditions on the validity of results will be recommended.

4. Evaluation of Pilot Program Field Procedures.

As all field collection of samples will be conducted on site by RMA personnel, it is proposed to serve as reviewers of and advisers to RMA on field techniques and to recommend modifications as indicated by the results of the validation study. The purpose of this activity is to assure that field techniques utilized will not adversely impact overall program quality control requirements.

C. Scope Modification

As a result of a joint meeting between RMA-IR and MALD, Edgewood Arsenal and Patterson Associates, Inc. personnel on January 19/20, 1977, eleven (11) specific compounds were designated for study in the proposed project. These were:

DCPD	p-Chlorophenyl methyl Sulfide
DIMP	p-Chlorophenyl methyl Sulfoxide
Aldrin	p-Chlorophenyl methyl Sulfone
Endrin	1, 4 - Dithiane
Isodrin	1, 4 - Thioxane
Dieldrin	

II. Review of Literature on Environmental Fates and Analytical Techniques

A. Introduction. A review of the recent literature was conducted, including chemical and analytical abstracts from 1967, for the specific compounds of interest exclusive of the chlorinated pesticides. The selective nature of this review was agreed upon in light of extensive work and established procedures for the soil analysis of these pesticides. The end result of this activity was the acquisition of extremely limited information on the specific compounds of interest (DIMP, DCPD, p-chlorophenylmethyl sulfide, p-chlorophenylmethyl sulfixide, p-chlorophenymethyl sulfone, dithiane and oxathiane (thioxane) with regard to soil and water behavior and analysis.

Furthermore, little information regarding compounds of similar chemical nature upon which one could extrapolate to the compounds of interest was found in these sources.

That information which was available resided principally in unpublished reports emmanating from contract or in-house studies under the direction of the U.S. Army. Still, minimal attention has been directed to the chemistry and analytical methodology for soils. Additional information has been obtained through direct communication with U.S. Army personnel and their contractors. This information has confirmed the absence of published literature, and limited information in unpublished literature, some of which may be unavailable due to security classification.

B. Results. A summary of the information obtained is presented below for each of the compounds.

1. Diisopropylmethylphosphonate (DIMP). No new references beyond those contained in USAMRDC Technical Report 7509, "Problem Definition Studies on Potential Environmental Pollutants II. Physical, Chemical, Toxicological and Biological Properties of 16 Substances," or their branching references were located. Other information is contained in the progress reports submitted to the U.S. Army, Fort Detrick, Maryland, by Aerojet Ordinance and Manufacturing Company under Contract DAMD-17-75-C-5069 by Dr. P. A. O'Donovan, personal communication with Dr. James Spigar

of Midwest Research Institute and apparently classified documents prepared by Midwest Research Institute under contract with an unidentified sponsor.

The essence of available information is that analysis of DIMP is without major problems and that its extraction from soils and plants appears to yield high recoveries. Aerojet researchers have found 90% recovery from spiked soil with a single methanol extraction. One gram of soil is contacted directly with methanol, agitated and centrifuged followed by direct solvent injection. Similar results have been indicated by Midwest Research Institute where other polar organic solvents such as iso-propanol, acetone and methanol have been used. No mention is made in either case regarding chloroform as the extractant, the solvent employed by RMA for extraction of water samples. The latter procedure has been found to yield essentially 100% recovery of DIMP at ppm levels (aqueous) with a volume ration of 67:1 ($H_2O:CHCl_3$).

The expected hydrolysis products, isopropylmethylphosphonic acid (or its salt), iso-propanol and methlyphosphonic acid (or its salt) may be of importance. While DIMP is estimated to be stable at neutral pH ($t_{1/2}$ = 687 years @ 10° C) this observation resulted from extrapolation of kinetic data obtained at elevated temperatures (80° - 98°C). However, at pH extremes, hydrolysis is significantly more rapid. No information was available regarding possible catalysis of the hydrolysis by metals or other constituents which may be present in the soil, including enzymatic mediation.

To delineate hydrolytic loss from other mechanisms resulting in low DIMP recovery from soil would necessitate specific analysis for the hydrolysis products. Communication with Midwest Research Institute indicates that extraction with polar solvents should provide appreciable recovery of IMP and MPA. Extraction with MeOH:H_2O (97:3) yielded 50% recovery on a single contact with spiked soil. Repeated extraction would likely enhance recovery. Furthermore, acidification may improve extraction efficiency but caution should be directed toward possible hydrolysis of IMP to MPA. MPA on the other hand would be expected to be stable to acidic conditions.

Analysis of extracted IMP and MPA has been reported by Midwest Research Institute to be readily achieved by sample evaporation, addition of ether and methylation by diazomethane. It should be noted that in this procedure, evaporative loss of DIMP is possible and analysis should be conducted on an aliquot of solvent directly for DIMP. Problems with this procedure have been noted and relate to the direct injection of the non-volatiles onto the column. MRI did not mention another potential problem, failure of the method to differentiate between the IMP and MPA species by GC.

Finally, tracer studies with ^{14}C methyl DIMP and DCPD are reportedly in progress at Aerojet. Greater detail is presented in the DCPD section below.

2. Dicyclopentadiene (DCPD). No information beyond that contained in USAMRDC Technical Report 7509, "Problem Definition Studies on Potential Environmental Pollutants II. Physical, Chemical, Toxicological and Biological Properties of 16 Substances," had been found in the published literature. The only other information relating to those aspects of this compound is contained in the Progress Reports

submitted to the U.S. Army, Fort Detrick, Frederick, Maryland, by Aerojet Ordinance and Manufacturing Company under Contract DAMD-17-75-C-5069, by Dr. P. A. O'Donovan.

Of particular note in this work are those studies pertaining to extraction from soils and gas chromatographic analysis. Based upon the results in reports 1953-01 (08), (15), (17), (18) MP, the following observations have been made:

Extraction Studies. Soils spiked with 340 ppm DCPD were extracted using 1 ml of hexane per gram of soil. Recoveries of DCPD averaged 52% for 8 samples. Lower recoveries were obtained with aqueous extractions (acidic, basic and neutral). It was reported that various solvents (unspecified) yielded a range of 18 to 80% of theoretical recovery.

Evaporation Studies. Decreased amounts of DCPD were found (recovered) after various periods of soil exposure to the atmosphere. These results were interpreted as indicating loss due to volatilization.

Radioactive Tracing. General ^{14}C labelled DCPD was introduced (homogeneously) into soil at 20 ppm and the soil was placed into pyrex test tubes to a depth of 4 inches. Dry air was passed over the soil surface at 100 ml/minute and then through two solvent traps in series (solvents unspecified) which were immersed in a dry ice/alcohol bath. Traps were removed after 8 and 50 hours (and longer, unspecified and assumed to be continuing at time of report). The traps and soil segments at 1 inch intervals were shipped to New England Nuclear (labelled compound supplier) for extraction and ^{14}C activity analysis. Preliminary results (reported in 1953-01 (19) MP, March 1977) from the Aerojet work have failed to yield definitive conclusions due to loss in activity between stock soil and working soil matrix. However, no further loss is indicated under test conditions. While the contractor does not wish to draw conclusions at this time, in the author's opinion the data are not supportive of volatilization loss of DCPD.

Gas Chromatography. While the specific analysis reported demonstrated linear relationships between DCPD and peak area, a dependency of sensitivity (ΔResponse/ΔConcentration) upon carrier gas flow rate (reported as inlet pressure) was found. Lower sensitivity was found at the lower inlet pressure. Since the flame ionization detector (FID) used is a mass flow rate detector, its response should be essentially independent of carrier gas flow rate. An implication is that partial degradation or conversion of the DCPD is occurring in the system, which would be expected to depend upon residence time. At least two causes for this could be projected. First, the column used was metal (stainless steel) which could catalyze reaction of the DCPD. The RMA procedure reported employs pyrex columns. Secondly, decomposition may occur independent of the column material, resulting from contact with the stationary phase. Either situation may produce an accumulation of degradation products on the column which may further enhance the breakdown of DCPD. In this case, the extent of breakdown could be a function of the period of column use and may be reversible or diminish upon period of non-use. Decomposition due to this process could greatly contribute to irreproducibility or results e.g. apparent erratic recoveries.

3. p-Chlorophenylmethyl Sulfide, Sulfoxide, Sulfone. The complete absence of literature on the aqueous and soil chemistry and

analysis of environmental samples for these compounds in the published literature was reported in personal communication by Dr. David Rosenblatt of Fort Detrick. This confirmed our experience in searching the literature.

Dr. Rosenblatt is currently assembling an information base on the chemical, physical, toxicological, and biological properties of these compounds.

4. Dithiane, Oxathiane (Thioxane). Our experience in searching the literature for pertinent information on these compounds reveals an absence of such information.

5. Related Compounds. While a significant body of literature exists for the extraction, analysis and environmental fate of compounds containing sulfur and phosphorus and compounds of general carbon skeleton similarity to DCPD, it is felt that dissimilarities in the absence of supporting information are sufficient to obviate extrapolation to compounds under study.

By the way of example, organophosphorus pesticides are phosphate esters rather than phosphonate esters and many of the phosphate esters contain sulfur in place of oxygen. Similarly, where sulfide, sulfoxide and sulfone functionality is encountered, e.g. Fenthian and its metabolites and degradation products, the presence of other functionalities precludes extrapolation of data for these compounds a priori to that of the compounds of concern.

For these reasons it was deemed necessary that an interim evaluation of the analytic methodologies be undertaken for each of the compounds to be studied in the pilot phase of the RMA comprehensive survey for the purpose of interim validation of sampling, handling and preservation methodology. This is necessary to ensure that the pilot phase of the Interim Geohydrological Pilot Program can proceed according to the time table established.

The development of final protocols is underway at Edgewood Arsenal. Interim protocols, based upon the recommendations below, are intended to be considered in conjunction and consultation with personnel from Edgewood Arsenal and Fort Detrick, and should be replaced where appropriate upon validation of final protocols for the subject compounds.

Additional Literature. Other selected articles obtained in the course of the specific literature that were deemed appropriate to the general nature of the problem were selected and transmitted to the RMA MALD personnel. A number of these articles were discussed with the ASC at the March 3 meeting and copies provided for the members. A list of these articles immediately follows this section.

The Environmental Protection Agency has just recently assembled a draft volume entitled Sampling and Analysis Procedures for Survey of Industrial Effluents for Priority Pollutants (March 1977). While not specifically germane to the compounds of interest, this document does contain recommended procedures for extraction, storage and emulsion breaking that may be of value to RMA personnel.

A copy of that document is appended to this report with the advisement that it is a preliminary document.

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2. J.J. Richard and G.A. Junk. Liquid Extraction for the Rapid Determination of Halomethanes in Water. J.AWWA 62-64 (1977).

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4. J.E. Henderson, G.R. Peyton and W.H. Glaze. A Convenient Liquid-Liquid Extraction Method for the Determination of Chloroform and Other Halomethanes in Water. Trace Analysis Laboratory, Institute of Applied Sciences, North Texas State University, Denton, Texas 76203.

5. E.A. Woolson. Extraction of Chlorinated Hydrocarbon Insecticides from Soil: Collaborative Study. J.AOAC Vol. 57, 604-609 (1974).

6. E.A. Woolson, and P.C. Kearney. Survey of Chlorinated Insecticide Residue Analyses in Soils. J.AOAC Vol. 52, 1202-1206 (1969).

7. J.G. Saha, Bharati Bhavaraju and Y.W. Lee. Validity of Using Soil Fortification with Dieldrin to Measure Solvent Extraction Efficiency. J. Agr. Food Chem. Vol. 17, 874-876 (1969).

8. J.H. Saha, Bharati Bhavaraju, Y.W. Lee and R.L. Randell. Factors Affecting Extraction of Dieldrin-^{14}C from Soil. J. Agr. Food Chem. Vol. 17, 877-882 (1969).

9. W.F. Tully. A Capillary Column for the Gas Chromatographic Analysis of Dicyclopentadiene. J. Chromatographic Sci. Vol. 9, 635-638 (1971).

10. R.R. Watts, R.W. Storherr, J.R. Pardue and T. Osgood. Charcoal Column Cleanup Method for Many Organophosphorus Pesticide Residues in Crop Extracts. J.AOAC Vol. 52, 522-526 (1969).

11. D.E. Coffin and G. Savary. Procedure for Extraction and Cleanup of Plant Material Prior to Determination of Organophosphate Residues. J.AOAC Vol. 47, 875-881 (1964).

12. L. Keay. The Preparation and Hydrolysis of Alkyl Hydrogen Methylphosphonates. Canad. J. of Chem. Vol. 43, 2637-2639 (1965).

13. F.C.G. Hoskin. Some Observations Concerning the Biochemical Inertness of Methylphosphonic and Isopropye Methylphosphonic Acids. Canad. J. of Biochem. and Physiol. Vol. 34, 743-746 (1956).

14. R.F. Hudson and L. Keay. The Hydrolysis of Phosphonate Esters. J. Chem. Soc. 2463-2469 (1956).

15. A. Bevenue, T.W. Kelley and J.W. Hylin. Problems in Water Analysis for Pesticide Residues. J. of Chromatog. Vol. 54, 71-76 (1971).

16. A. Hubaux and G. Vos. Decision and Detection Limits for Linear Calibration Curves. Anal. Chem. Vol. 42, 849-855 (1970).

17. W.L. Dilling, N.B. Tefertiller and G.J. Kallos. Evaporation Rates and Reactivities of Methylene Chloride, Chloroform, 1,1,1-Trichloroethane, Trichloroethylene, Tetrachloroethylene, and Other Chlorinated Compounds in Dilute Aqueous Solutions. Env. Sci. Tech. Vol. 9, 833-387 (1975).

18. N.M. Karayannis, C. Owens, L.L. Pytlewski and M.M. Labes. Diisopropyl Methylphosphonate Complexes of Metal Perchlorates. J. Inorg. Nucl. Chem. Vol. 31, 2059-2071 (1969).

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22. W.E. Harris and B. Kratochvil. Sampling Variance in Analysis for Trace Components in Solids. Anal. Chem. Vol. 46, 313-314 (1974).

23. C.M. Menzie. Metabolism of Pesticides. Special Scientific Report--Wildlife No. 127, Washington, D.C. (1969).

24. C.M. Menzie. Metabolism of Pesticides. Special Scientific Report--Wildlife No. 184, Washington, D.C. (1974).

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III. Recommended Interim Validation Protocols

As a result of preliminary evaluation and subsequent meeting with RMA, Fort Detrick, Edgewood Arsenal and other members of the Analyt ical Systems Committee on March 2 and 3, 1977, a set of recommendations were made and an experimental sequence was designed to develop and assess an analytical methodology for the eleven compounds selected. This initial recommendation is presented below.

A. Initial Recommendations

While assessment of mass balances using radioactively tagged compounds would be the method of choice, such studies are not feasible within the time frame of the project and appear to be prohibitively expensive based upon the work of Dr. O'Donovan of Aerojet.

The validity of spiking soil samples to assess extraction efficiencies is of constant concern. Any procedure that does not represent the natural uptake mechanism of a compound onto the soil is of questionable reliability in the evaluation of solvent extraction efficiency for recovery of soil contaminants. In spite of these potential problems, some assessment of soil extraction efficiency is necessary and the following recommended procedures are intended to screen potentially useful extraction procedures with well-defined soils deemed likely to represent the worst conditions likely to occur at RMA and provide some measure of the recovery under conditions closely approximating those of actual field samples.

There are three aspects to this study, each designed to yield information about the potential utility of solvents to be used for extraction of the individual compounds from the pilot study program soil samples. Close control of methodology and full characterization of each phase is intended in order to provide retroactive comparison of interim methodologies with procedures ultimately developed by Edgewood Arsenal.

Phase 1. Solvent Screening. The intent of the following procedures is to evaluate the potential loss of the individual compounds irreversibly onto the study soils directly from extraction solvents. While this procedure will not differentiate between irreversible binding and compound transformation if less than 100% recovery is achieved, it will serve as a first step in assessing solvent acceptability and will thus diminish the effort required in the following phases.

Two separate soil types will be utilized, one of high clay content and one of high organic content. It is felt that these two soil types represent the worst expected conditions. The clay soil selected should be that most likely to present difficulty in compound recovery and should by finally selected in concert with Dr. Timofeeff and representatives of the Analytical Systems Committee, especially those from Edgewood Arsenal.

Sufficient quantities of soil should be acquired and processed to allow complete conduct of the tests outlined under this section (III), studies of sampling, handling and preservation methodology validation (Section IV) and future studies with final methodologies emmanating from Edgewood Arsenal to allow comparison of interim procedures results with the results of final methods. From these latter undertakings, significant differences in the two methods can at least yield data correction factors to be applied retroactively.

Details of specific homogenization methods to ensure uniformity of the study soils and individual sub-sample removal procedures to ensure representation of the whole sample in each study phase should be in harmony with accepted procedures and be approved by the ASC. Soil samples are to be sieved to provide full information regarding particle size distribution and the smallest particle size compatible with acceptable solvent flow through soil columns should be utilized. Alternatively, small particle sizes are to be used but blended with material of low compound uptake of sufficient size to yield manageable flow rates through the columns.

Samples of the final soil systems should have surface area per unit mass evaluations made. Availability of these determinations through Edgewood Arsenal was indicated at the March 3rd ASC meeting.

For each soil, each of the following compounds:

Aldrin	p-chlorophenylmethyl sulfide
Dieldrin	p-chlorophenylmethyl sulfoxide
Endrin	p-chlorophenylmethyl sulfone
Isodrin	Dithiane
DCPD	Oxathiane (Thioxane)
DIMP	

will be dissolved in the solvent under study in concentration sufficient to assure easy and reproducible analytical detection. A known volume of the solvent/compound solution will be applied to the surface of a 5-inch column of soil (known moisture content, to be determined separately) as a lense. Pure solvent is then to be passed through the column at a slow flow rate (measured) and 6 fractions of 20 ml each are to be collected and analyzed for the individual compound by gas chromatography. A blank, control column for each soil and solvent system should be run to evaluate extraction of substances from the soil that might interfer with compound analysis.

If interfering substances are eluted, clean-up procedures must be developed and conventional techniques could be evaluated directly on the blank or control column eluents. A cross check of the clean-up procedures on pure compound solutions (not applied to columns) should then also be made to assure no compound loss through clean-up.

Rapid and essentially complete passage of the individual compounds through the column should strongly indicate the potential utility of the solvent system for field soil sample extraction and be subjected to Phase 3 studies for final evaluation.

Tentative solvents are as follow:

Chlorinated Pesticides	(a) hexane/acetone (1:1) (b) chloroform/methanol (1:1)
DIMP	(a) methanol (b) chloroform
DCPD	(a) methylene chloride (b) carbon disulfide
Sulfur Compounds	(a) chloroform (b) acetone

Phase 2. Aqueous Uptake Assessment

It is intended that spiked soil samples for direct extraction efficiency assessment be prepared by the uptake of compound directly from aqueous solution, thereby simulating natural uptake. Quantitation of the individual compound loading on the study soils (those of Phase 1 above) is fundamental to evaluation of extraction recoveries.

To evaluate the feasibility of this method of spiking, small scale studies for each compound for each of the soil types will be conducted as follow:

Aqueous solutions of known concentration for each compound (near saturation for those compounds of low solubility) will be contacted with known weights of soil (5g soil to 250 ml of solution) for 24 hours with agitation. Minimal head space conditions are to be maintained with sealed flasks. After appropriate solids separation, the residual concentration in the aqueous phase will be determined. High losses to the soli phase are sought and expected for most compounds and if achieved, additio solution contact will be made to achieve adequate loadings on the soil.

Failure to obtain significant transfer to the soil would imply that field samples would be expected to have low uptake of the materials from solution (directly but not as the result of interstitial water evaporation). Under this condition, evaporative spiking might be better justified.

Given adequate uptake, a mechanism for spiking has been achieve that likely reflects the actual field samples and allows quantitation c the soil content of the individual compounds. Additionally, informatior regarding the partitioning of the compound between the aqueous phase anc the soil will have been obtained which will be of value in transport assessment and modelling.

To obtain sufficient spiked soil for extraction efficiency eval ation, the procedures would be repeated on large volumes of soil and solution in mechanically stirred carboys. These soil samples would als be employed in Section IV upon successful extraction solvent evaluation.

Phase 3. Solvent Extraction Efficiency Assessment

Soils spiked by procedures of Phase 2 and thus of known compound content should be drained by gravity to essentially field capacity. Actual moisture content is to be evaluated for each sample. Known wet weights of soil for each compound will be subjected to batch extraction with the solvents of Phase 1 (or their replacements if not suitable) to evaluate recovery efficiency. If efficiencies are less than 90% additional extractions should be undertaken to determine if low recovery is due to poor partitioning into the solvent or loss of the compound onto the soil (irreversible binding or compound degradation). Up to three batch extractions should be made (assuming satisfactory detection limits).

For repeated extractions yielding reproducible stepwise recoveries of appreciable amount but total recovery of less than 90%, soxhlet extractions should be evaluated for enhanced recovery.

It is to be noted that if acceptable recoveries are obtained, actual processing of samples may be undertaken by column elution of samples rather than batch extraction or soxhlet pending the results of the above studies.

B. Results Based on Initial Recommendations

1. Background

The studies outlined in the initial recommendations (A. above) had not been completed at the time of this report. In some instances, discontinuation and/or modification of these recommendations was instituted. Implementation of recommended interim analytical protocols required extensive analytical development which has not been completed within the projected time frame of this project. A combination of factors is responsible for this problem. These include:

(a) Manpower. Originally projected increases in MALD staffing which were intended in part to support the methods of development at work, did not occur. Furthermore, while MALD has not undergone any direct manpower reduction, RMA has undergone and is continuing to undergo a reduction in force exceeding 50% of total personnel. Such processes and attendent perturbations are always accompanied by reductions in work efficiency related to personnel morale even among those not directly affected.

(b) Priorities Establishment. Within existing manpower availability, other activities such as analysis of routine samples for water monitoring, Quality Control Assessment and special short term intensive studies have been given higher priority than the Validation Program. The large analytical load required for these projects has limited analyses of samples for the Validation Program Studies and consequently has contributed to the delay in achieving the original objectives. Other nonanalytical delays, related to man power have occurred, including soil acquisition and processing, and have also contributed to this delay.

Acquisition of additional staff, as originally planned, would have allowed achievement of the original project goals without interfering with laboratory priorities, therefore problems 1 & 2 are interrelated in their impact on the project.

(c) Analytical Difficulties. Further aggravation of the problem in achieving the goals of the proposed Validation program and main taining the projected timetable relates to specific difficulties in routin analytical procedures caused by instrumentation unreliabilities and inadequacies. The former, potentially an interface problem between GC and the computer system which should be resolved by the vendor. The latter, lack of adequate gas flow control on the flame photometric sulfur detector, is being resolved by installation of constant flow controllers.

The end result of these analytical problems has been to greatly increase the time and manpower required per analysis and therefore to decrease the rate of attainment of the Validation results.

2. MALD Study Results

Those results from the 3 phases originally recommended are presented below in conjunction with indications as to where procedures differed from initial experimental design.

(a) Phase 1. Solvent Screening. Only results from the clay soils have been received formally but verbal communication indicated that similar behavior occurred. For the clay soil, columns of clay soil were loaded with 60 $\mu g/60_g$ of the individual compounds in a particular solvent as a lense and then flushed through the column. Fractions collected were analyzed for the compound and mass recovery was computed. Results of this work, as reported to the contractor, are given in Table III-1. MALD personnel speculate that low recoveries for some of the chlorinated pesticides relate to analytical interferences since the collected solvent had not been subjected to clean up procedures prior to analysis. Additional comment relative to the high recoveries suggested solvent evaporation during sample collection as a concentration factor leading to slightly high values.

MALD has indicated that clean up procedures are to be investigated for all compounds to be extracted from soils.

Based upon preliminary results in clay soil and heavy analytical demands, further solvent screening was not conducted.

TABLE III-1. COMPOUND RECOVERIES FROM CLAY SOIL COLUMNS.

Compound	Solvent	% Recovered
Aldrin	Hexane/Acetone	52
Isodrin	Hexane/Acetone	94
Dieldrin	Hexane/Acetone	72
Endrin	Hexane/Acetone	>100
DIMP	Chloroform	104
DCPD	Methylene Chloride	113
Thioxane	Chloroform	97
Dithiane	Chloroform	106
p-Chlorophenyl methyl Sulfide	Chloroform	110
p-Chlorophenyl methyl Sulfoxide	Chloroform	102
p-Chlorophenyl methyl Solfone	Chloroform	103

Compound loadings were 1μg per gram of soil in the column.

(b) Phase 2. Aqueous Uptake Assessment. Rather than work individually with the eleven compounds, MALD elected to work directly with the Carboy scale and all eleven compounds combined.

For preparation of the spiked water, excess quantities of each compound were added to 19 liters of distilled water and the system was then stirred for 24 hours. Gravity filtration and compound analysis by established water analysis procedures yielded the results in Table III-2, (first column). Duplicate analyses were performed.

Two soil samples, (1 organic & 1 clay), were contacted with an 8-liter portion of the aqueous solution for 24 hours and the aqueous phase was analyzed after gravity separation of the suspended soil. These results are also given in Table III-2.

Significant uptakes of the chlorinated pesticides by both soils is indicated. Little uptake of DIMP was observed. Similar observations apply to thioxane on both soils and dithiane on clay.

While high uptake of p-chlorophenyl methyl sulfide is indicated upon initial examination, low uptakes of the sulfone and sulfoxide in most cases and much greater than 100% recovery from solution in one case suggest oxidation is occurring in solution or at the soil surface. Additional study was implemented for these compounds.

Following similar procedures, the individual compounds were spiked in aqueous solution yielding concentrations of 84.5, 102.7 and 105.0 µg/l respectively for the sulfide, sulfoxide and sulfone. Contact with soil at 31.25 g/l distilled water (125g/4 liter for sulfide, 25g/800 ml for sulfoxide and sulfone) for 24 hours has been conducted. No data have been supplied.

The existing data indicate first that adsorption from aqueous solution is not likely to be an effective spiking procedure for the sulfoxide and the sulfone.

TABLE III-2. SOIL SPIKING EXPERIMENTAL RESULTS.
(All concentrations in μg/l).

Compound	Initial Water Concentrations Raw	Initial Water Concentrations Avg.	Water Concentration After Contact with Soil. Clay Raw	Clay Avg.	Organic Raw	Organic Avg.
Aldrin	4.57 5.98	5.28	N.D.	N.D.	1.17 1.56	1.39
Isodrin	3.18 3.45	3.32	0.42 0.43	0.42	1.24 1.39	1.32
Dieldrin	6.77 6.70	6.74	2.05 2.14	2.10	N.D.	N.D.
Endrin	11.3 11.9	11.6	3.54 3.59	3.56	N.D.	N.D.
DIMP	105 107	106	103 96.0	99.5	97.1 110	103
DCPD	60.3 71.1	65.7	Concentrations too low to allow reproducible results.			
1,4-Thioxane	126 127	126	109 105	107	106 108	107
1,4-Dithiane	95 95	95 95	72 80	76	55 55	55
p-chlorophenyl methyl sulfide	106 107	106	26 28	27	N.D.	N.D.
p-chlorophenyl methyl solfoxide	117 118	118	115 114	114	153 156	154
p-chlorophenyl methyl sulfone	111 111	111	108 114	111	103 107	105

While initial examination of the sulfide behavior would suggest that effective spiking was achieved, other evidence (phase 3) indicates that the compound is converted to the sulfoxide and/or sulfone in solution.

(c) Phase 3. Solvent Extraction Efficiency Assessment. The original 11 compound "spiked soil" was subjected to initial recovery studies. These data are summarized in Table III-3. At the time of report preparation, exact details of the extraction procedures had not been supplied for this table. However, because of the phase 2 results and problems associated therewith, the results in Table III-3 are of diminished importance at this time. Especially since there are clear indications of interferences in the analytical procedure for chlorinated organics with the organic soils and general recovery problems with all of the sulfur containing compounds.

(d) Additional Studies. Attempts to develop a single soil extraction solvent for all compound analyses using chloroform with subsequent azeotope distillation with a suitable alkane were attempted. Results for standard water samples containing only the chlorinated pesticides are presented in Tables III-4 and III-5. These results would tend to favor use of dual extraction, expecially if the polytron method to be mentioned below proves effective. The azeotrope does not seem to sufficiently eliminate the chloroform to the point of not interfering with the electron capture detector.

C. Additional Recommendations

Based on results obtained to date for the development of Interim Validation Protocols, the following are recommended.

TABLE III-3. SUMMARY OF EXTRACTION RECOVERY FROM COMPOSITE SPIKED SOIL

	DIMP	Aldrin	Isodrin	Endrin	Dieldrin	Sulfide	Sulfoxide	Sulfone	Dithiane	Thioxane
A. Clay Soil										
Initial Aq Soln	$8.5x10^5$	$4.2x10^4$	$2.7x10^4$	$9.3x10^4$	$5.4x10^4$	$8.5x10^5$	$9.4x10^5$	$8.9x10^5$	$7.6x10^5$	$1.0x10^6$
Final Aq. Soln	$8.0x10^5$	0	0	0	$7.6x10^3$	0	$9.1x10^5$	$8.9x10^5$	$6.1x10^5$	$8.6x10^5$
%uptake on soil	5.9	100	100	100	85.2	0	3.2	0	19.7	14.0
Amount on soil	$5 x10^4$	$4.2x10^4$	$2.7x10^4$	$9.3x10^4$	$4.6x10^4$	$8.5x10^5$	$3.0x10^4$	0	$1.5x10^4$	$1.4x10^5$
Amount recovered from soil	$2.6x10^4$	$6.2x10^4$	$1.9x10^4$	$6.5x10^4$	$4.9x10^4$	$1.9x10^4$	$3.6x10^4$	$4.6x10^4$	$1.1x10^4$	$2.9x10^5$
% recovery	52	150	70	70	106	2.2	120	—	14	21
ng/g lost on soil	96	—	32	110	—	3300	0	0	560	440
B. Organic Soil										
Initial Aq. Soln	$8.5x10^5$	$4.2x10^4$	$2.7x10^4$	$9.3x10^4$	$5.4x10^4$	$8.5x10^5$	$9.4x10^5$	$8.9x10^5$	$7.6x10^5$	$1.0x10^6$
Final Aq. Soln	$7.6x10^5$	$1.1x10^4$	0	0	0	0	$1.23x10^6$	$8.4x10^5$	$4.4x10^5$	$8.6x10^5$
% uptake on soil	10.6	73.8	100	100	100	100	-31	5.6	42.1	14.0
Amount on Soil	$9.4x10^4$	$3.1x10^4$	$2.7x10^4$	$9.3x10^4$	$5.4x10^4$	$8.5x10^5$	—	$5x10^4$	$3.2x10^5$	$1.4x10^5$
Amount recovered from soil	$3.3x10^4$	$7.2x10^4$	$2.6x10^4$	$1.4x10^5$	$1.1x10^5$	$1.9x10^5$	—	$6.5x10^4$	$1.5x10^4$	$1.7x10^4$
% recovery	37	230	96	151	204	22	—	130	21	12
ng/g lost on soil	230	—	4	—	—	2600	—	—	1200	490

TABLE III-4 AZEOTROPE DISTILLATION STUDIES WITH HEXANE.

Sample A1	AVG area	ng/ml conc.	% recovery based on Std.
Aldrin	256481	427	90.1
Isodrin	115270	209	38.8
Dieldrin	232868	418	81.5
Endrin	94227	309	61.7
Sample A2			
Aldrin	238908	398	84.0
Isodrin	101909	185	34.3
Dieldrin	196378	359	70.0
Endrin	95146	311	62.1
Sample A3			
Aldrin	240379	401	84.7
Isodrin	121350	220	40.9
Dieldrin	208681	379	73.9
Endrin	107870	346	69.1

average area of $CHCl_3$ in samples was $3x10^7$.

TABLE III-5 AZEOTROPE DISTILLATION STUDIES WITH ISO-OCTANE

Sample HS-700	AVG area	Conc. ng/ml	% recovery based on HS-700
Aldrin	298552	461	
Isodrin	274182	461	
Dieldrin	269956	458	
Endrin	131830	453	
Sample H1-700			
Aldrin	233278	360	78.1
Isodrin	215616	362	78.5
Dieldrin	204976	348	76.0
Endrin	101774	349	77.0
Sample H2-700			
Aldrin	237393	367	79.6
Isodrin	219153	368	79.8
Dieldrin	207760	353	77.1
Endrin	104800	360	79.5

$CHCl_3$ present in the extracts.

1. In light of the previously discussed low uptake from aqueous solution of compounds by soil and the attendant uncertainty in the loading of these compounds on soil, the percent extraction recovery as determined by MALD is subject to a large propagated error. Consequently, although it is not the most desireable methodology, it is recommended that direct spiking of soil be accomplished by addition of compound(s) in a suitable organic solvent. Subsequent extraction of such soil samples will provide a value for the maximum extraction efficiency. These spiking studies should utilize both wet and dry soil samples as indicated in Reference 8 of Section II, page 12. Based on results of comparative Soxhlet and Polytron extraction efficiency, the use of the polytron is recommended. Data from these studies can be compared with those which have been obtained on the samples for which the compounds had been supplied from aqueous solution.

2. Based on the results of the analysis of soil samples, in particular those for pesticides in which there were apparent recoveries in excess of 100%, it is recommended that clean-up procedures be adopted. A primary reason for such clean-up is the removal of interfering compounds from the sample. In the development of clean-up procedures, the recovery of the compounds to be analyzed must be determined to validate the appropriateness of the cleanup procedure. Another important reason for the utilization of clean-up procedures is the reduction of possible degradation or reaction of the compounds of interest in the inlet or on the column due to catalysis by or reaction with other compounds. To establish the significance of such reaction in the absence of clean-up and their elimination by appropriate clean-up measures, it is recommended

that analysis of extracts and of extracts which have been spiked with a known amount of compound be conducted. If the analytical sensitivity (slope of calibration curve or response factor) is found to be the same for spiked samples as it is for standards, this is indicative that no interference has been encountered. Finally, if an appropriate internal standard can be found, its use in the analytical procedure should be adopted. An appropriate internal standard is a compound of similar physicochemical characteristics to the analytes but which is absent in the environmental samples. It must produce a unique chromotographic peak. The internal standard should be added to the soil sample prior to extraction.

These comments apply particularly to the sulfur species but cannot be overlooked for DIMP.

3. Conflicting experiences by RMA-MALD and Aerojet personnel as to the stability of DCPD ammended soils and solutions and the preliminary results of this study with regard to uptake of DCPD by soil and its subsequent recovery from the soil casts doubt on the meaningfulness of DCPD analyses on soils. Until such time as adequate methodology has been developed it is recommended that analysis of DCPD in soil not be conducted.

4. If clean up procedures and standards additions do not resolve the recovery problems with the sulfur compounds, the p-chlorophenyl methyl compounds should be reported as a lumped value in weight of sulfur. For the Thioxane and Dithiane, if low recoveries can not be attributed to analytical interferences, the current time limitations

preclude further developmental work. Values determined with existing methodology will simply have to be recorded for the pilot study with future reevaluation based on final methods development from Edgewood Arsenal.

5. Evaluation of the polytron system should be made with the spiked soils since this system will be essential to sample processing requirements in light of section IV recommendations.

IV. Validation of Sampling, Handling and Preservation Methodology

A. Initial Recommendations

Subsequent to establishing the required extraction, clean-up and analysis interim protocols as described above, Section B, these protocols will be used in the validation of sampling, handling and preservation methods for the Pilot Soil/Water Sampling Program. Of paramount importance is the determination of the time course for recovery of compounds from stored soil samples. Both spiked soil samples and homogenized core sample horizons should be studied. Storage periods of up to 90 days, under refrigerated and ambient temperature conditions should be used and fractions of the soils should be taken for extraction and analysis after 1, 3, 7, 14, 28, 60 and 90 days. The samples should be stored in sealed containers. In addition, samples should be stored in trays to evaluate the effect of maximum atmospheric exposure.

B. Final Recommendations

In light of problems discussed in the previous section, the recommendations of A above cannot be accomplished. Therefore, it is recommended that immediate extraction of soil samples be practiced, commensurate with EPA recommendations. Solvent solutions after extraction should be stored at -15°C until analysis can be accomplished.

Quite clearly, this will necessitate that the rate of drilling in the study be regulated by MALD's ability to process samples through the extraction stage. While not desireable, in the absence of information to the contrary, the soil cores must be assumed to be unstable with respect to the compounds of interest.

V. Evaluation of Pilot Program Field Procedures

In light of program delays and failure of the original time table relative to interim methods development, activity in this task could not be addressed even after a 60 day extention of the original contract duration, as no cores had been drilled to that time.

APPENDIX A

SAMPLING AND ANALYSIS PROCEDURES FOR SURVEY OF INDUSTRIAL EFFLUENTS FOR PRIORITY POLLUTANTS

SAMPLING AND ANALYSIS PROCEDURES FOR

SURVEY OF INDUSTRIAL EFFLUENTS FOR PRIORITY POLLUTANTS

U.S. ENVIRONMENTAL PROTECTION AGENCY

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY

CINCINNATI, OHIO 45268

MARCH 1977

FOREWORD

These guidelines for sampling and analysis of industrial wastes have been prepared by the staff of the Environmental Monitoring and Support Laboratory, at the request of the Effluent Guidelines Division, Office of Water and Hazardous Wastes, and with the cooperation of the Environmental Research Laboratory, Athens, Georgia. The procedures represent the current state-of-the-art but improvements are anticipated as more experience with a wide variety of industrial wastes is obtained. Users of these methods are encouraged to identify problems encountered and assist in updating the test procedures by contacting the Environmental Monitoring and Support Laboratory, EPA, Cincinnati, Ohio 45268.

Collection of Samples

1. Collection of Composite Samples for Liquid-Liquid Extraction

Collect a 72 hour composite sample. The maximum time interval between aliquot samples shall be no longer than 30 minutes. The minimum aliquot size shall be 50 ml. The sample must be collected with an automatic sampler using the equipment and methods outlined below. Minimum composite volume must be 2 1/2 gallons.

Automatic Sample Collection

Sampler - A peristaltic pump automatic sampler with timer and a single glass compositing jug is required. The 2 1/2 - 3 gallon compositing bottle must be glass and cleaned as outlined below. New unused tubing must be used for the sampling line and for the pump for each individual outfall or sample location. Vacuum type automatic samplers may be used provided that the sample chambers are glass and that they are cleaned after every use as outlined for glass composite containers. For raw discharges, the velocities in the sample line should approach 2 feet per second. Place the sampler or composite sample container in an insulated chest and ice. Maintain the sample at 4°C during the compositing procedure. At the completion of the compositing period seal the 2 1/2 - 3 gallon compositing container with a teflon lined cap. Place the compositing container in an insulated shipping container, ice, and seal according to chain of custody procedures, then ship to the analytical laboratory. Maintain at 4°C during transport and storage prior to analysis.

When more than one laboratory is involved in the analysis of the various parameters, the sample should be divided in the field. For purposes of this survey, divide the composite sample into three parts: one for metals analysis, one for pesticide analysis, and one for GC/MS compound survey.

Directions for the Field Division of the Composite Sample - Blend the composite sample to provide a homogeneous mixture including a representative suspension of any solids in the container. No specific method is required, hand stirring with clean glass or Teflon rods, mechanical paddles or magnetic mixing with Teflon coated stirring bars may be used. Metal mixing devices may not be used.

Metals - Withdraw a well blended aliquot of the composite sample. Using a glass funnel, rinse the sample container with a small portion of the sample, then transfer 1-liter of sample to the bottle. Preserve with 1 ml of concentrated nitric acid. Seal and prepare for shipment as described above

Pesticides - Withdraw three liters of well-blended sample, then using a glass funnel transfer the sample to a narrow mouth one-gallon glass bottle that has been prepared in the same manner as the composite sample container. Seal with a Teflon lined cap and prepare for shipment as described above.

GC/MS Sample - Seal the remaining sample in the composite container or other appropriate size glass bottle and prepare for shipment as described above.

Field Blank Procedure for Automatic Samplers

Blank Water - Blank water must be as free from organic interferences as possible. The analytical laboratory should supply this water in bulk glass containers (minimum of five li for field use. The supplying laboratory shall analyze the blank water to determine the organic background that may be present.

Procedure - All tubing and other parts of the sampling system must be scrubbed with hot detergent water and thorough rinsed with tap water and blank water prior to use. Further rinsing with interference free acetone and methylene chloride is advised when tubing and other parts permit, i.e., are not susceptible to dissolution by the solvent. [Note: Tygon plastic tubing is a source of phthalate ester contamination. Where its use is required, i.e., in the peristaltic pump, the length must be kept as short as possible. Teflon is acceptable and may be used in other parts of the sampling system as required.] Cut the sampler tubing to length at the laboratory, but do not install on the equipment. In the field, pump two liters of blank water through the sampling line and pump tubing and discard. Then pump three liters of blank water through the system and collect as a blank in a 1-gallon sample bottle that has been prepared as described below. Seal the bottle with a Teflon lined cap. Immediately ice the blank (4°C) and maintain at (4°C) during transport and storage prior to analysis.

Composite Container - Prepare narrow-mouth 3 gallon glass sample bottles for use by washing with hot detergent water and thoroughly rinsing with tap water and blank water. Heat the bottles at 400°C in a muffle-furnace or dry heat sterilizer for 30 minutes or alternatively, rinse with interference free acetone and methylene chloride and air dry at room temperature protected from atmospheric or other sources of contamination. Caps for the bottles must be lined with Teflon which has been solvent rinsed as above.

2. Collection of Grab Samples

Collect grab samples (a minimum of one per day) for the analysis of phenol, cyanide, mercury and volatile organics (purgable). Collect samples from the raw process discharge, the treated effluent, and the treated effluent after chlorination, when chlorination is practiced. It is recommended that the samples be collected from mid-channel at mid-depth.

Samples should be collected at a turbulent, well mixed section of the channel.

Cyanide (Total)

Container - Use new one-liter plastic bottles that will not contaminate the sample. Wash the bottles and caps with hot detergent water and thoroughly rinse with tap water and blank water.

Collect a 1-liter sample.

Preservation - At the time of collection, add 2 ml of 10 N sodium hydroxide per liter (pH $\leq$12). Oxidizing agent such as chlorine decompose most of the cyanides. Test a drop of the sample at the time of collection with potassium iodide starch test paper (KI-starch paper); a blue color indicates the need for treatment. Add ascorbic acid, a few crystals at a time, until a drop of the sample produces no color on the indicator paper. Then add an additional 0.6 g of ascorbic acid for each liter of sample volume.

Seal the sample bottles and place in an insulated chest and ice (4°). Seal the chest and ship to the analytic laboratory. Maintain at 4°C during transport and storage (out of light) prior to analysis.

Mercury

Container - Use new 1-liter plastic bottles cleaned before use as described in "Methods for Chemical Analysis of Water and Wastes," paragraph 4.1, page 81, 1974 (see Appendix IV). Rinse the bottle with a portion of sample prior to filling with sample.

Collect a one-liter sample.

Preservation - At time of collection, acidify the sample by addition of redistilled, concentrated nitric acid (5 ml/l). After acid addition, mix and check pH with pH paper having a range of 1 to 12. If pH is not 2 or below, add more acid until pH 2 is reached. The volume of additional acid should be noted on the sample tag. (Maximum holding time under these conditions is six months.) Seal the sample bottles, place in shipping container, seal and ship to the analytical laboratory.

<u>Phenols</u>

Container - Use new one-liter glass bottles. Wash the bottle and Teflon cap liner with hot detergent water and thoroughly rinse with tap water and blank water.

Collect a 1-liter sample.

Preservation - At time of collection, acidify the sample by addition of phosphoric acid or sulfuric to pH 4. Note volume of acid added on sample tag. Seal bottle, place in insulated chest and ice (4°C). Seal chest and ship to analytical laboratory. Maintain at 4°C during transport and storage (out of light) prior to analysis.

Volatile Organics (Purge and Trap Method).

Containers - Use 45 ml screw cap glass vials with Teflon faced silicone septa:

Vials[a] - Pierce #13074 or equivalent

Septa[a] - Pierce #12722 or equivalent

Wash the bottles, septa, and caps with hot detergent water and thoroughly rinse with tap water and blank water. Heat the bottles and septa at 105°C for one hour, cool to room temperature in an enclosed contaminant free area. When cool, seal bottles with septa (Teflon side down) and screw cap. Maintain the bottles in this condition until just prior to filling with blank water or sample.

Collect duplicate 45 ml samples each time samples are collected, i.e., once during each day for three days. Two blank water samples, sealed in 45 ml vials, are to accompany the sample bottles during shipment to and from the sampling site. If preservation is to be used, collect four samples dur each sampling period. Two should be preserved and two not preserved. Two preserved and two non-preserved blanks are to be provided.

(a) Available from Pierce, Inc., Box 117, Rockford, IL 61105

Filling and Sealing Bottles - Slowly fill each container to overflowing. Carefully set the container on a level surface. Place the septum (Teflon side down) on the convex sample meniscus. Seal the sample with the screw cap. To insure that the sample has been properly sealed, invert the sample and lightly tap the lid on a solid surface. The <u>absence</u> of entrapped air bubbles indicates a proper seal. If air bubbles are present, open the bottle, add additional sample, and reseal. The sample must remain hermetically sealed until it is analyzed.

Preservation - Preservative (sodium thiosulfate or sodium bisulfite) is used to stabilize samples containing residual chlorine. The production of chloroform and other haloforms continues in such samples if they are not stabilized. Waste streams that have been treated with chlorine should be tested on site to determine whether or not preservative is needed. If preservation is required, collect both preserved and non-preserved samples. Wrap the samples with water proof packing material, place in an insulated chest and ice at 4°C. Maintain at 4°C during transport and storage prior to analysis.

3. <u>Identification of Samples</u>

All samples and blanks <u>must</u> be carefully identified using water proof labels and waterproof ink. Include the following information on the label: sample number, date and hour of sampling, complete information as to source and sampling point, preservative added, if any, and name of person collecting the sample (include address and/or phone number).

Volatile Organics (Purge and Trap Method)

1. Scope

This method is designed to determine those "unambiguous priority pollutants", associated with the Consent Decree, that are amenable to the purge and trap method. These compounds are listed in Table I of this section. It is a gas chromatographic/mass spectrometric method intended for qualitative and semi-quantitative determination of these compounds during the survey phase of the industrial effluent study.

Certain compounds, acrolein and acrylonitrile, are not efficiently recovered by this method and should be determined by direct aqueous injection gas chromatography. Direct aqueou injection GC is recommended for all compounds that exceed 1000 µg/l.

2. Special Apparatus and Materials

Sample extraction apparatus (minimum requirements):

5-ml glass syringes with Luer-Lok - 3 each

2-way syringe valves (Teflon or Kel-F) - 3 each

8 inch, 20 gauge syringe needle - 2 each

5-ml glass, gas-tight syringe, pressure-lok[(a)] or equivalent - 1 each

Tekmar Liquid Sample Concentrator, model LSC-1 or equivalent[(b)]. Includes a sorbent trap

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(a) Available from Precision Sampling Corp., P.O. Box 15119, Baton Rouge, LA 70815

(b) Available from Tekmar Company, P.O. Box 37202, Cincinnati, OH 45222.

consisting of 1/8 in. O.D. (0.09 to 0.105 in. I.D.) x 6 in. long stainless steel tube packed with 4 inches of Tenax-GC (60/80 mesh) and 2 inches of Davison Type-15 silica gel (35/60 mesh).

3. <u>Gas Chromatographic Column Materials</u>

Stainless steel tubing 1/8 in. O.D. (0.09 to 0.105 in. I.D.). Carbopack C (60/80 mesh) coated with 0.2% Carbowax 1500. Supelco stock No. 1-1826.[c] Chromosorb-W (60-80 mesh) coated with 3% Carbowax 1500.

4. <u>Procedure</u>

Preparation of Standards -- Prepare standard stock solutions (approximately 2 μg/μl) by adding, from a 100 μl syringe, 1 to 2 drops of the 99+% pure reference standard to methanol (9.8 ml) contained in a tared 10 ml volumetric flask (weighed to nearest 0.1 mg). Add the compound so that the two drops fall into the alcohol and do not contact the neck of the flask. Use the weight gain to calculate the concentration of the standard. Prepare gaseous standards, i.e., vinyl chloride, in a similar manner using a 5 ml valved gas-tight syringe with a 2 in. needle. Fill the syringe (5.0 ml) with the gaseous compound. Weight the 10 ml volumetric flask containing 9.8 ml of methyl alcohol. Lower the syringe needle to about 5 mm <u>above</u> the methyl alcohol

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(c) Available from Supelco, Supelco Park, Bellefonte, PA 16823 meniscus. Slowly inject the standard into the flask. The gas rapidly dissolves in the methyl alcohol. Reweigh the flask, dilute to volume, mix, tightly stopper, and store in a freezer. Such standards are generally stable for at least one week when maintained at less than 0°C. Stock standards of compounds which boil above room temperature are generally stable for at least four weeks when stored at 4°C.

[Safety Caution: Because of the toxicity of most organohalides, primary dilutions must be prepared in a hood. Furthe it is advisable to use an approved respirator when handling high concentration of such materials.]

From the primary dilution prepare a secondary dilution mixture in methyl alcohol so that 20.0 µl of the standard, diluted to 100.0 ml in organic free water, will give a standar which produces a response close to that of the unknown. Also prepare a complex test mixture at a concentration of 100 ng/µ containing each of the compounds to be determined. Prepare a 20 µg/l quality check sample from the 100 ng/µl standard by dosing 20.0 µl into 100.0 ml of organic free water.

Internal Standard Dosing Solution - From stock standard solutions prepared as above, add a volume to give 1000 µg eac of bromochloromethane, 2-bromo-1-chloropropane, and 1,4-dichlorobutane to 45 ml of organic free (blank water) contair in a 50 ml volumetric flask, mix and dilute to volume. Prep a fresh internal standard on a weekly basis. Dose the internal standard mixture into every sample and reference standard analyzed.

Preliminary Treatment of Sample - Remove samples from cold storage (approximately an hour prior to analysis) and bring to room temperature by placing in a warm water bath at 20-25°C.

Purging and Trapping Procedure - Adjust the helium purge gas flow to 40 ml/min. Set the Tekmar 2-way valve to the purge position and open the purging device inlet. Remove the plungers from two 5-ml syringes and attach a closed 2-way syringe valve to each. Open the sample bottle and carefully pour the sample into one of the syringes until it overflows. Replace the syringe plunger and compress the sample. Open the syringe valve and vent any residual air while carefully adjusting the volume to 5.0 ml. Then close the valve. Fill the second syringe in an identical manner from the same sample bottle. Use the second syringe for a duplicate analysis as needed. Open the syringe valve and introduce 5.0 µl of the internal standard mixture through the valve bore, then close the valve. Attach the 8 inch needle to the syringe valve and inject the sample into the purging device. Seal the purging device and purge the sample for 12 minutes. The purged organics are sorbed on the Tenax-silica gel trap at room temperature (20-25°C).

While the sample is being purged, cool the gas chromatographic column oven to near room temperature (20-30°C). To do this, turn heater off and open column oven door.

At the completion of the 12 minute purge time, inject the sample into the gas chromatograph by turning the valve to the desorb position. Hold in this position for four minut while rapidly heating the trap oven to 180°C, then return the valve to the purge position, close the GC column oven door, and rapidly heat the GC oven to 60°C. Hold at 60°C for four minutes, then program at 8°/minute to 170°C and hold until all compounds have eluted. Begin collecting GC/MS data as soon as the GC/MS vacuum system has stabilized ($<10^{-5}$ torr).

While the sample is being chromatographed, flush the purging device with two 5-ml volumes of organic free water. Then bake out the trap to minimize the amount of water desorb into the GC/MS system during the succeeding injection step. [Note: If this bake out step is omitted, the amount of water entering the GC/MS system will progressively increase causing deterioration of and potential shut down of the system.]

GC/MS Determination - The analytical conditions for determination of the volatile priority pollutants amenable to purge and trap, using the Tekmar LSC-1 and the computerized Finnigan 1015 GC/MS are given below:

Purge Parameters

Purge gas - Helium, high purity grade

Purge time - 12 minutes

Purge flow - 40 ml/min.

Trap dimensions - 1/8 in. O.D. (0.09 to 0.105 in. I.D.) x 6 in. long

Trap sorbent - Tenax-GC 60/80 mesh (4 in.) plus Type 15 silica gel (35/60 mesh)

Desorption flow - 20 ml/min.

Desorption time - 4 min.

Desorption temperature - 180°C

Gas Chromatographis Parameters

Column - Stainless steel, 8 ft. long x 1/8 in. O.D. (0.09 to 0.105 in. I.D.) packed with Carbopack C (60/80 mesh) coated with 0.2% Carbowax 1500, preceded by a 1 ft. x 1/8 in. O.D. (0.09 to 0.105 in. I.D.) packed with Chromosorb-W coated with 3% Carbowax 1500.

Carrier gas - Helium at 33 ml/min.

Oven temperature - Room temperature during trap desorption, then rapidly heat to 60°C, hold at 60° C for four minutes, then program to 170°C at 8°/minute. Hold at 170° C for 12 minutes or until all compounds have eluted.

Mass Spectrometer Parameters

Data System - System Industries System 150

Separator - glass jet

Electron energy - 70 ev

Emission current - 500 ua

Ion energy - 6 volts

Lens voltage - (-)100 volts

Extractor voltage - 8 volts

Mass range - 20-27, 33-260 amu

Integration time/amu - 17 milliseconds

Samples/amu - 1

Gas Chromatographic Column Conditioning Procedure - Attach the Carbowax 1500-Chromosorb end of the column to the inlet system of the gas chromatograph. Do not, at this time, attach the column exit to the detector. Adjust the helium flow rate through the column to 33 ml/minute. Allow the column to flush with helium for ten minutes at room temperat then program the oven from room temperature to 190 °C at 4°/minute. Maintain the oven at 190° C overnight (16 hours).

Handle the column with extreme care once it has been conditioned because the Carbopack is fragile and easily fract Once fractured, active sites are exposed resulting in poor peak geometry (loss of theoretical plates). Reconditioning , generally, revitalizes the analytical column. Once properly conditioned, the precolumn may be removed.

The retention data listed in Table I was collected with the precolumn in the system.

Quality Assurance - The analysis of blanks is most important in the purge and trap technique since the purging device and the trap can be contaminated by residues from very concentrated samples or by vapors in the laboratory. Prepare blanks by filling a sample bottle with low-organic water (blank water) that has been prepared by passing distilled water through a pretested activated carbon column. Blanks should be sealed, stored at 4°C, and analyzed with each group of samples.

After each sample analysis, thoroughly, flush the purging device with blank water and bake out the system. Subsequently, analyze a sample blank (one that has been transported to and from the sampling site). If positive interferences are noted, analyze a fresh laboratory sample of blank water. If positive interference still occurs, repeat the laboratory blank analysis. If interference persists, dismantle the system, thoroughly, clean all parts that the sample comes into contact with and replace or repack the sorbent trap and change carrier gas.

Precision - Determine the precision of the method by dosing blank water with the compounds selected as internal standards - bromochloromethane, 2-bromo-1-chloropropane, and 1,4-dichloromethane - and running replicate analyses. These compounds represent early, middle, and late retention times over the range of the Consent Decree compounds and are not, themselves, included on the list. Construct Quality Control charts from the data obtained according to directions in Appendix VI.*

The sample matrix can affect the purging efficiencies of individual compounds, therefore, each sample must be dosed with the internal standards and analyzed in a manner identical to the internal standards in blank water. When the results of the dosed sample analyses show a deviation greater than two sigma, repeat the dosed sample analysis. If the deviation is again greater than two sigma, dose another aliquot of the same sample with the compounds of interest at approximately two times the measured values and analyze. Calculate the recovery for the individual compounds using these data.*

Calibration of the gas chromatography-mass spectrometry (GC-MS) system - Evaluate the system performance each day that it is to be used for the analysis of samples or blanks. Inject a sample of 20 nanograms of decafluorotriphenylphosphine[(d)] and plot the mass spectrum. The criteria in Appendix III must be met and all plots from the performance evaluation, documented and retained as proof of valid performance.

(d) Available from PCR, Inc., Gainesville, FL

* See Reporting of Data Section. p. 11.

Analyze the 20 μg/l standard to demonstrate instrument performance for these compounds.

Qualitative and Quantitative Determination - The characteristic masses or mass ranges listed in Table II of this section are used for qualitative and quantitative determination of volatile priority pollutants. They are used to obtain an extracted ion current profile (EICP)[e] for each compound. For very low concentrations, the same masses may be used for selected ion monitoring (SIM)[f]. The primary ions to be used to quantify each compound are also listed. If the sample produces an interference for the primary ion, use a secondary ion to quantify.

Quantify samples by comparing the response of the unknown in a sample to that of a standard. When positive responses are observed, prepare and analyze a reference standard so that the standard response closely approximates the sample response. Calculate the concentration in the sample as follow

$$\frac{\dfrac{\text{(Response for unknown)}}{\text{(Response for standard)}}}{\text{Concentration of standard } (\mu g/l)} = \mu g/l \text{ of unknown}$$

5. Reporting of Data

Report all results to two significant figures or to the nearest 10 μg/l. Report internal standard data to two significant figures.

(e) EICP is the reduction of mass spectrometric data acquired by continuous, repetitive measurement of spectra by plotting the change in relative abundance of one or several ions as a function of time.

(f) SIM is the use of a mass spectrometer as a substance selective detector by measuring the mass spectrometric response at one or several characteristic masses in real time.

As the analyses are completed, transfer GC-MS data onto magnetic tape as described under reporting of data in method for "Semivolatile Organics by Liquid-Liquid Extraction.

Report all quality control (QC) data along with the analytical results for the samples. In addition, forward all QC data to EMSL, Cincinnati.

6. Direct Aqueous Injection Gas Chromatography

As noted in the Scope, Acrolein and acrylonitrile should be analyzed by direct aqueous injection gas chromatography. References to these methods are given in Appendix VII. The detection level for these methods is 0.1 mg/l and above.

Table I

Elution Order of Volatile Priority Pollutants[a]

Compound	RRT[b]	Method Recovery (percent)	Modified Method Recovery (percent)[c]
chloromethane	0.152	91	
dichlorodifluoromethane	0.172	0	100
bromomethane	0.181	85	
vinyl chloride	0.186	101	
chloroethane	0.204	90	
methylene chloride	0.292	76	
trichlorofluoromethane	0.372	96	
1,1-dichloroethylene	0.380	97	
bromochloromethane(IS)	0.457	88	
1,1-dichloroethane	0.469	89	
trans-1,2-dichloroethylene	0.493	92	
chloroform	0.557	95	
1,2-dichloroethane	0.600	98	
1,1,1-trichloroethane	0.672	94	
carbon tetrachloride	0.684	87	
bromodichloromethane	0.750	92	
1,2-dichloropropane	0.818	92	
trans-1,3-dichloropropene	0.847	90	
trichloroethylene	0.867	89	
dibromochloromethane	0.931	87	
cis-1,3-dichloropropene	0.913	85	
1,1,2-trichloroethane	0.913	88	
benzene	0.937	no data	
2-bromo-1-chloroethane(IS)	1.000	92	
bromoform	1.115	71	
1,1,2,2-tetrachloroethene	1.262	88	
1,1,2,2-tetrachloroethane	1.281	58	
1,4-dichlorobutane(IS)	1.312	74	

Compound	RRT[b]	Method Recovery (percent)	Modified Method Recovery (percent)[c]
toluene	1.341	no data	
chlorobenzene	1.489	89	
ethylbenzene	1.814	no data	
acrolein	unknown	12	74
acrylonitrile	unknown	no data	

(a) These data were obtained under the following conditions: GC column - stainless steel, 8 ft. long x 0.1 in. I.D. packed with Carbopack C (60/80 mesh), coated with 0.2% Carbowax 1500; preceeded by a 1 ft. long x 0.1 in. I.D. column packed with Chromosorb W coated with 3% Carbowax 1500; carrier flow - 40 ml/ oven temperature - initial 60°C held for 3 min., programmed 8°C/ to 160°C and held until all compounds eluted.

(b) Retention times relative to 2-bromo-1-chloropropane with an absolute retention time of 829 seconds.

(c) No measurable recovery using standard purging and trapping conditions. Under modified conditions, i.e., purging at 10 ml/min for 12 min., recovery is 100%.

(d) Recovery 12% under standard purging conditions, i.e., room temperature, 30% at 55°C, and 74% at 95°C.

Table II

Characteristic Ions of Volatile Organics

Compound	EI Ions (Relative intensity)	Ion used to quantify
chloromethane	50(100); 52(33)	50
dichlorodifluoromethane	85(100): 87(33); 101(13);103(12)	101
bromomethane	94(100); 96(94)	94
vinyl chloride	62(100); 64(33)	62
chloroethane	64(100); 66(33)	64
methylene chloride	49(100); 51(33); 84(86); 86(55)	84
trichlorofluoromethane	101(100); 103(66)	101
1,1-dichloroethylene	61(100); 96(80); 98(53)	96
bromochloromethane(IS)	49(100); 130(88) 128(70); 51(33)	128
1,1-dichloroethane	63(100); 65(33); 83(13); 85(8); 98(7); 100(4)	63
trans-1,2-dichloroethylene	61(100); 96(90); 98(57)	96
chloroform	83(100); 85(66)	83
1,2-dichloroethane	62(100); 64(33); 98(23); 100(15)	98
1,1,1-trichloroethane	97(100); 99(66); 117(17); 119(16)	97
carbon tetrachloride	117(100); 119(96); 121(30)	117
bromodichloromethane	83(100); 85(66); 127(13); 129(17)	127
1,2-dichloropropane	63(100); 65(33); 112(4); 114(3)	112
trans-1,3-dichloropropene	75(100); 77(33)	75
trichloroethylene	95(100); 97(66) 130(90); 132(85)	130
dibromochloromethane	129(100); 127(78) 208(13); 206(10)	127
cis-1,3-dichloropropene	72(100); 77(33)	75

Compound	EI Ions (Relative intensity)	Ion used to quantify
1,1,2-trichloroethane	83(95); 85(60); 97(100); 99(63); 132(9); 134(8)	97
benzene	78(100)	78
2-bromo-1-chloroethane(IS)	63(100); 65(33); 142(14); 144(18)	142
bromoform	171(50);173(100); 250(4); 252(11); 254(11); 256(4)	173
1,1,2,2-tetrachloroethene	129(64); 131(62); 164(78); 166(100)	164
1,1,2,2-tetrachloroethane	83(100); 85(66); 131(7); 133(7); 166(5); 186(6)	168
1,4-dichlorobutane(IS)	55(100); 90(21); 92(7)	90
toluene	91(100); 92(78)	92
chlorobenzene	112(100); 114(33)	112
ethylbenzene	91(100); 106(33)	106
acrolein	26(49); 27(100); 28(5); 29(43); 55(64); 56(83)	56
acrylonitrile	26(100); 51(32); 52(75); 53(99)	53

Semivolatile Organics by Liquid-Liquid Extraction

1. Scope

This method is designed to determine those "unambiguous priority pollutants" associated with the Consent Decree, that are solvent extractable and amenable to gas chromatograp! These compounds are listed in Tables I to III of this section Except for the pesticides, it is a gas chromatographic-mass spectrometric method intended for qualitative and semi-quantitative determination of these compounds during the survey phase of the industrial effluent study. Pesticides are initially determined by electron capture-gas chromatograp and, qualitatively, confirmed by mass spectrometry.

2. Special Apparatus and Materials

Separatory funnels - 2 and 4 l with Teflon stopcock

Continuous liquid-liquid extractors - any such apparatu designed for use with solvents heavier than water and having a capacity of 2 to 5 l[a] (Aldrich Catalog No. Z10, 157-5). Connecting joints and stopcocks must be of Teflon or glass with no lubrication.

3. Procedure

Sample Preparation for GC-MS Survey - Blend the composite sample to provide a homogeneous mixture including

(a) Available from Aldrich Chemical Co., Milwaukee, WI a representative portion of the suspended solids that are present. - No specific method is required but a motor driven mechanical stirrer with a propeller type blade is suggested. Stirring with metal devices is acceptable for organic sampling.

Transfer the sample from the composite container through a glass funnel into a 2-liter graduated cylinder and measure the volume. Then transfer to a 4-liter separatory funnel or a continuous extractor as described below. Rinse the cylinder with several portions of the first volume of extracting solvent. [Note: Either separatory funnel or continuous extraction is acceptable for isolation of the organics. Continuous extraction must be used when emulsions cannot be broken. See discussion under Emulsions.]

Base-Neutral Extraction

Separatory Funnel Extraction - Adjust the pH of the sample with 6 N NaOH to 11 or greater. Use multirange pH paper for the measurement. Serially extract with 250 x 100 x 100 ml portions of distilled-in-glass methylene chloride. (About 40 ml of the first 250 ml portion will dissolve in the sample and not be recovered.) Shake each extract for at least 2 min. by the clock.

Dry and filter the solvent extract by passing it through a short column of sodium sulfate. Concentrate the solvent by Kuderna-Danish (K-D) evaporation (distillation). The sodium sulfate should be prewashed in the column with methylene chloride. [Note: Check sodium sulfate blank and, if necessary, heat in an oven at 500°C for 2 hours to remove interfering organics.] After drying the extract, rinse the sodium sulfate with solvent and add to the extract.

Evaporate the extract to 5-10 ml in a 500 ml K-D apparat fitted with a calibrated receiver tube. Allow the K-D to coo to room temperature. Remove the receiver, add fresh boiling chips, attach a two-chamber micro-Snyder column and carefully evaporate to 1.0 ml or when active distillation ceases. Remove the micro-Snyder column and add the internal standard: 10 µl of 2 µg/µl d_{10}-anthracene (per each ml of extract). Mi thoroughly.

If it is to be overnight or longer before the extract is run by GC-MS, transfer it from the K-D ampul with a disposabl pipet to a solvent tight containers. The recommended contai is a standard 2 ml serum vial with a crimp cap lined with teflon coated rubber. These are inert and methylene chlorid can be held without evaporation loss for months if caps are unpierced. When the extracts are not being used for analysi store them with unpierced caps in the dark and at refrigerat or freezer temperatures.

Acid (Phenols) Extraction - Adjust the pH of the base-neutral extracted water with 6 N HCl to 2 or less. Seriall extract with 200 x 100 x 100 ml portions of distilled-in-gl methylene chloride. (Note that only 200 ml is used for the first extraction). Proceed as described for the base-neutral extract, including the addition of the internal st

Emulsions - The recovery of 85% of the added solvent will constitute a working definition of a broken emulsion. (You may correct the recovery of the first portion for water solubility of methylene chloride.) Any technique that meets this criteria is acceptable. Among techniques that have been tried on these samples with fair success are:

1. Centrifugation of the emulsion layer after removal of any separated solvent.
2. Passage of the emulsion through a column plugged with a ball of methylene chloride-wet glass wool. The solvent used to wet the wool and to wash it after the emulsion goes through must be measured and subtracted from the total volume to determine 85% recovery.
3. Relative to labor, solvent is cheap. The addition of excess solvent sometimes breaks weak emulsions. You must remember to use excess solvent in the blanks also.
4. Let the emulsion stand for up to 24 hrs.
5. Draw off the small amount of free solvent that separates and slowly drip it back in the top of the separatory funnel and through the sample and emulsion.

Other ideas include stirring with a glass rod, heating on a steam bath, addition of concentrated sodium sulfate solution, and sonication.

Continuous Extraction - If you cannot achieve 85% solvent recovery, start with a fresh aliquot of sample and extract by continuous extraction.

Adjust the pH of the sample as appropriate, pour into the extractor, and extract for 24 hours. When extracting a 2-liter sample, using the suggested equipment, two liters of blank water must be added to provide proper solvent recycle

For operation, place 200-300 ml of solvent in the extractor before the sample is added and charge the distillin flask with 500 ml of solvent. At the end of the extraction remove the solvent from the distilling flask only and evapora and treat as described in the base-neutral extract section.

Blank Extraction: It is not entirely certain that 2 liters of blank will always be available. When it is, proceed to process it as the corresponding sample was done. Include any emulsion breaking steps that used glass wool, excess solvent or additional chemicals. If less than 2 lite: is available, measure the blank and bring it to volume with distilled water. On analysis make the necessary quantitative corrections.

Pesticides: These compounds are to be analyzed by EC-GC using the EPA method published in the Federal Register Vol. 38, Number 125, Part II, pp. 17318-17323. (Friday, June 29, 1973). One-liter rather than 100 ml is to be extracted. The solvent amounts given in the method and other parameters remain unchanged. If pesticides are found by EC, the extract is to be carefully evaporated (clean airstream) to 0.5 ml and sent for GC-MS confirmation.

The compounds to be analyzed by EC-GC are listed in Table I of this section

If the pesticide sample has been received in a 1-gal. bottle, hand shake the bottle for 1 min. by the clock to evenly suspend sediment. Pour the sample into a 1-liter graduated cylinder and measure the volume. Then transfer the sample to a 2-liter separatory funnel and rinse the cylinder with the first volume of extracting solvent. Use additional small volumes of solvent if necessary to transfer all of the sample. Proceed with the extraction using the solvents and amounts prescribed in the published method.

If the sample is to be taken from the original composite bottle, homogeneously mix as described earlier and transfer a 1-liter aliquot to a graduated cylinder, then trasnfer to the separatory funnel with the aid of a glass funnel and rinse the cylinder as above.

If intractable emulsions are encountered that cannct be broken as described in the GC-MS survey section, then a fresh 1-liter sample should be processed in a continuous extractor using methylene chloride as the solvent as described earlier but without pH adjustment. The methylene chloride will have to be evaporated to a small volume and exchanged into hexane for clean-up or EC-GC analysis. To do this, evaporate the methylene chloride to 6 to 8 ml, cool, add 20 ml of hexane and a fresh boiling stone and re-evaporat to the desired analytical volume (5 ml or less).

Final storage and transport of sample extracts: After analysis, the extracts of the base-neutrals, acids, blanks and pesticides are to be sent to ERL, Athens, Ga 30601, ATTN: Dr. Walter Shackelford.

Each extract is to be washed out of its container into a 10 ml glass ampul and brought to 5 ml ± 1 ml. Methyle chloride is the solvent for the base-neutrals and acids, hexane for pesticides. The ampuls are to be sealed in a rounded-off, fire polished manner, i.e., no thin sharp peaks of glass that are easily broken on handling and shipping. After sealing the ampuls, put an indelible mark at the solvent level. Securely attach a label or tag that gives:

Type of fraction (base-neutral, etc.)
Industrial category
Name (of plant, city and state)
Specific source or stage of treatment
Date sampled originally
Date sealed
Name of contractor and analytical laboratory

Wrap the ampuls in packing material to prevent breakage and mail or ship them postpaid at ambient temperature. When the samples are safely in ampuls, the remainder of the composite sample may be discarded.

4. GC-MS Analysis

Compounds to be analyzed by GC-MS alone fall into two categories--those in the base-neutral extract (Table II) and those in the acid extract (Table III). Pesticides (Table I) that were tentatively identified in the pesticide analysis will be confired by GC-MS.

The base-neutral extractables may be separated and eluted into the MS under the following chromatographic conditions:

Column--6 foot, 2.0 mm inside diameter, glass
Packing--1% SP2250 on 100/120 mesh, Supelcoport
Program--hold 4 minutes @ 50°, program 50°-260° @ 8°/min.
hold 20 minutes @ 260°
Injector--275°
Separator--275°
Carrier gas--He @ 50 ml/min
Injection size--$\geq$2 µl

Table II lists the 49 base-neutral extractable compounds in order of relative retention times (compared to hexachlorobenzene) for the above GC conditions. Detection limits were determined by MS response. The seven compounds without retention times or limits of detection were not available for this report. It is not recommended that 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) be acquired due to its extreme toxicity. Based on their similarity to compounds that were available all seven are expected to be chromatographable using these standard conditions. In addition the characteristic masses recommended for MS identification are listed in Table II.

The limits of detection given in Tables I and II refer to the quantity necessary to inject to get confirmation by the MS methods described below.

At the beginning of each GC-MS run of a base-neutral extract, the operator should demonstrate the ability to chromatograph benzidine at the 40 ng level. Only after this is accomplished should the run be started. If benzidine can be chromatographed, the other nitrogen-containing compounds of Table II can be chromatographed as well.

If desired, capillary or SCOT columns may be used instead of the packed column of SP-2250. Coatings of OV-17 or SP-2250 may be used. The elution order of OV-17 and SP-2250 are very similar. Some specific data for OV-17 is given in Table V. The performance criteria for benzidine must still be met and in addition, the system must be shown to elute the late running polynuclear aromatic compounds.

The acid extractables may be chromatographed as follows:

Column--6 foot, 2.0 mm inside diameter, glass
Packing--Tenax GC, 60/80 mesh
Program--180° - 300° @ 8°/min
Injector--290°
Separator--290°
Carrier Gas--He @ 30 ml/min
Injection size--$\geq$ 2 µl

Table III lists the 11 acid extractables in order of relative retention times (compared to 2-nitrophenol). Chromatography of nitrophenols is poor. The limits of detection given refer to the amounts required to get MS confirmation by the methods described below.

Before an acid extract is run on the GC-MS the operator should demonstrate the ability to detect 100 ng of pentachlorophenol.

Mass spectrometry should be conducted with a system utilizing a jet separator for the GC effluent since membrane separators lose sensitivity for light molecules and glass frit separators inhibit the elution of polynuclear aromatics. A computer system should be interfaced to the mass spectrometer to allow acquisition of continuous mass scans for the duration of the chromatographic program. The computer system should also be equipped with mass storage devices for saving all data from GC-MS runs. There should be computer software available to allow searching any GC-MS run for specific ions and plotting the intensity of the ions with respect to time or scan number. The ability to integrate the area under any specific ion plot peak is essential for quantification.

To indicate the presence of a compound by GC-MS, three conditions must be met. First, the characteristic ions for the compound (Tables I-III) must be found to maximize in the same spectrum. Second, the time at which the peak occurs must be within a window of ± 1 minute for the retention time of this compound. Finally, the ratios of the three peak heights must agree with the relative intensities given in Tables I-III within ± 20%.

An example of identifying a component is as follows:

It is known that hexachlorobenzene elutes from the SP2250 column at 19.4 minutes. Hexachlorobenzene has characteristic mass ions at 284(100%), 142(30%), and 249(24%). The computer is asked to display a plot of the intensities of these ions versus time (or MS scan number) and the window from 18.4-20.4 minutes is examined for the simultaneous peaking of the intensities of these ions. If all three ions are present, the ratio of the peak heights is checked to verify that it is 100:30:24 ± 20%. If the three tests are successful, hexachlorobenzene has been identified in the sample.

Table I lists the 18 pesticides and PCB's that will be confirmed by GC-MS using the SP2250 column. Chlordane, toxaphene and the PCB's have retention ranges rather than specific times due to their being multicomponent mixtures. It is suggested that the first 14 materials be confirmed exactly as the other base-neutral compounds.

The last four materials require special treatments. Chlordane is expected to produce two main peaks within the retention range given in which all three masses listed will maximize. Toxaphene will produce several (5-15) peaks in which the masses given will maximize within the retention time range. For the PCB's each mass given corresponds to the molecular ion of PCB isomers, e.g., 294 is tetrachlorobiphenyl. A specific mass plot will show multiple peaks for each of these ions within the retention time listed, but in general they will not maximize in the same TIC peak. For these four materials in particular it is necessary to also run a standard. Because GC-MS is only being used for confirmation--and at its limit of detection--all quantification will

will be done by EC-GC for the pesticides. The methods for these four are not final and feedback from the field to Dr. Shackelford is welcome.

When a compound has been identified, the quantification of that compound will be based on the integrated area from the specific ion plot of the first listed characteristic ion in Tables II and III. Quantification will be done by the internal standard method using deuterated anthracene. Response factors, therefore, must be calculated to compare the MS response for known quantities of each priority pollutant with that of the internal standard. The response ratio (R) may be calculated as:

$$R = \frac{Ac}{Aa} \times \frac{Ca}{Cc}$$

where Ac is the integrated area of the characteristic ion from the specific ion plot for a known concentration, Cc. Aa and Ca are the corresponding values for deuterated anthracene. The relative response ratio for the priority pollutants should be known for at least two concentration values--40 ng to approximate 10 ppb and 400 ng to approximate the 100 ppb level. Those compounds that do not respond at either of these levels may be run at concentrations appropriate to their response. For guidance in MS limits of detection refer to the values given in Tables I-III.

The concentration of a compound in the extract may now be calculated using:

$$C = \frac{Ac \times Ca}{R}$$

where C is the concentration of a component, Ac is the integrated area of the characteristic ion from the specific ion plot, R is the response ratio for this component, Aa is the integrated area of the characteristic ion in the specific ion plot for deuterated anthracene, and Ca is the concentration of deuterated anthracene in the injected extract.

In samples that contain an inordinate number of interferences the chemical ionization (CI) mass spectrum may make identification easier. In Tables II and III characteristic CI ions for most compounds are given. The use of chemical ionization MS to support EI is encouraged but not required.

5. Quality Assurance

GC-MS system performance evaluation is required each day the system is used for samples or reagent blanks. A sample of 20 ng of decafluorotriphenylphosphine[(b)] is injected into the system and the mass spectrum is acquired and plotted. Criteria established in Appendix III must be met. The analyst must also demonstrate that the analytical conditions employed result in sharp total ion current peaks for 40 ng of benzidine on the SP2250 column when this column is used and 100 ng of pentachlorophenol on the Tenax GC column when it is used with the MS as a detector. All plots from the performance evaluation must be retained as proof of valid performance.

As performance evaluation samples become available from EMSL-Cincinnati, they are to be analyzed by solvent extraction once each 20 working days and the results reported with other analytical data.

The 1% SP2250 and Tenax GC column packings are available by request to EPA contractors from Dr. Walter Shackelford, EPA, Aghens, GA.

(b) Available from PCR, Gainesville, FL

Standards for the priority pollutants may be obtained from the sources listed in Appendix IX. Those compounds marked with an asterisk have not yet been received by the Athens laboratory.

In order to minimize unnecessary GC-MS analysis of blanks, the extract may be run on a FID-GC equipped with appropriate SP2250 and Tenax GC columns. If no peaks are seen of intensities equal to or greater than the deuterated anthracene internal standard then it is not necessary to do a GC-MS analysis. If such peaks are seen, then the blank must be sent for full priority pollutant analysis.

The contractor will look for all priority pollutants to the limit of 10 µg/l except in those cases listed in Tables II-III in which limits of detection are too high for analysis at this level.

6. Reporting of Data

All concentrations should be reported in ranges--10 ppb - 100 ppb and greater than 100 ppb. Report concentrations for pesticides as prescribed in the Federal Register Method. The relative response ratios from MS analysis should be included when reporting d:

All GC-MS data is to be saved on 9-track magnetic tape and sent to the Athens Environmental Research Laboratory for storage and later evaluation. The tape format is:

Type--9-track, 800 BPI, 2400 foot reels
Record length--80
Block Size--≤ 4000 (specify)
Code--EBCDIC

An acceptable data format would have the first two records containing the sample identification. Subsequent records contain eight mass-intensity pairs, each of which is 5 characters long and left justified. At the end of each spectrum in a sample run, the last mass-intensity pair is blank to denote the end of the spectrum. When all data for the run is on the tape, an end-of file mark should be written. The next sample run can then be entered. One example is:

2 Records: Sample 1 identification
N Records: Spectrum 1 of sample, last mass-intensity pair is blank to denote end of spectrum
M Records: Spectrum 2 of sample, last mass-intensity pair is blank to denote end of spectrum
.
.
.
L Records: Spectrum N of sample, last mass-intensity pair is blank to denote end of spectrum
END OF FILE
2 Records: Sample 2 identification
etc.

Other data formats are possible, but <u>any</u> format that is used <u>must</u> be accompanied by a full explanation of all record formats.

All magnetic tapes, documentation and a table of MS response ratios should be sent to:

Dr. W. M. Shackelford
Athens Environmental Research Lab
College Station Road

Table II. Base-ı ıtral Extractables

Compound Name	RRT[1] (hexachloro-benzene)	Limit of Detection (ng)	Characteristic EI ions (Rel. Int.)	CI ions (Methane)
1,3-dichlorobenzene	0.35	40	146(100), 148(64), 113(12)	146, 148, 150
1,4-dichlorobenzene	0.36	40	146(100), 148(64), 113(11)	146, 148, 150
hexachloroethane	0.38	40	117(100), 199(61), 201(99)	199, 201, 203
1,2-dichlorobenzene	0.39	40	146(100), 148(64), 113(11)	146, 148, 150
bis(2-chloroisopropyl) ether	0.47	40	45(100), 77(19), 79(12)	77, 135, 137
hexachlorobutadiene	0.55	40	225(100, 223(63), 227(65)	223, 225, 227
1,2,4-trichlorobenzene	0.55	40	74(100), 109(80), 145(52)	181, 183, 209
naphthalene	0.57	40	128(100), 127(10), 129(11)	129, 157, 169
bis(2-chloroethyl)ether	0.61	40	93(100), 63(99), 95(31)	63, 107, 109
hexachlorocyclopentadiene	0.64	40	237(100), 235(63), 272(12)	235, 237, 239
nitrobenzene	0.64	40	77(100), 123(50), 65(15)	124, 152, 164
bis(2-chloroethoxy)methane	0.68	40	93(100), 95(32), 123(21)	65, 107, 137
2-chloronaphthalene	0.76	40	162(100), 164(32), 127(31)	163, 191, 203
acenaphthylene	0.83	40	152(100), 153(16), 151(17)	152, 153, 181
acenaphthene	0.86	40	154(100), 153(95), 152(53)	154, 155, 183
isophorone	0.87	40	82(100), 95(14), 138(18)	139, 167, 178
fluorene	0.91	40	166(100), 165(80), 167(14)	166, 167, [illegible]
2,6-dinitrotoluene	0.93	40	165(100), 63(72), 121(23)	183, 211, [illegible]
1,2-diphenylhydrazine	0.96	40*	77(100), 93(58), 105(28)	185, 213, 225
2,4-dinitrotoluene	0.98	40	165(100), 63(72), 121(23)	183, 211, 223
N-nitrosodiphenylamine	0.99	40*	169(100), 168(71), 167(50)	169, 170, 19[illegible]
hexachlorobenzene	1.00	40	284(100), 142(30), 249(24)	284, 286, [illegible]
4-bromophenyl phenyl ether	1.01	40	248(100), 250(99), 141(45)	249, 251, 277
phenanthrene	1.09	40	178(100), 179(16), 176(15)	178, 179, 207
anthracene	1.09	40	178(100), 179(16), 176(15)	178, 179, 207
dimethylphthalate	1.10	40	163(100), 164(10), 194(11)	151, 163, 164
diethylphthalate	1.15	40	149(100), 178(25), 150(10)	177, 223, 251
fluoranthene	1.23	40	202(100), 101(23), 100(14)	203, 231, 243
pyrene	1.30	40	202(100), 101(26), 100(17)	203, 231, 243
di-n-butylphthalate	1.31	40	149(100), 150(27), 104(10)	149, 205, 279
endosulfan sulfate	1.41	20 μg	272(100), 387(75), 422(25)	421, 423, 425
benzidine	1.38	40*	184(100), 92(24), 185(13)	185, 213, 225
butyl benzylphthalate	1.46	40	149(100, 91(50)	149, 299, 327

Compound Name	RRT[1] (hexachlorobenzene)	Detection Limit (ng)	Characteristic EI ions (Rel. Int.)
β-endosulfan	0.51	40	201(100), 283(48), 278(30
α-BHC	1.02	40	183(100), 109(86), 181(91
γ-BHC	1.09	40	183(100), 109(86), 181(91
β-BHC	1.12	40	181(100), 183(93), 109(62
aldrin	1.14	40	66(100), 220(11), 263(73)
heptachlor	1.15	40	100(100), 272(60), 274(46
heptachlor epoxide	1.23	40	355(100), 353(79), 351(60
α-endosulfan	1.24	40	201(100), 283(48), 278(30
dieldrin	1.28	40	79(100), 263(28), 279(22)
4,4'-DDE	1.30	40	246(100), 248(64), 176(65
4,4'-DDD	1.33	40	235(100), 237(76), 165(93
4,4'-DDT	1.38	40	235(100), 237(72), 165(59
endrin	1.41	40	81(100), 82(61), 263(70)
δ-BHC			183(100), 109(86), 181(90
chlordane	1.14-1.37		373(19), 375(17), 377(1[illegible]
toxaphene	1.22-1.47		(231, 233, 235)*
PCB-1242	0.93-1.24		(224, 260, 294)*
PCB-1254	1.18-1.41		(294, 330, 362)*

* These ions are listed without relative intensities since the mixtures they represent defy characterization by three masses.

** These three ions are characteristic for the α and γ forms of chlordane. No stock should be set in these three for other isomers.

1 1% SP-2250 on 100/120 mesh Supelcoport in a 6' x 2 mm id glass column; He @ 30 ml/min; Program: 50° for 4 min, then 8°/min to 260° and hold for 15 min.

Table II. Base-neutral Extractables (Cont'd.)

Compound Name	RRT[1] (hexachloro-benzene)	Limit of Detection (ng)	Characteristic EI ions (Rel. Int.)	CI ions (Methane)
chrysene	1.46	40	228(100), 229(19), 226(23)	228, 229, 257
bis(2-ethylhexyl)phthalate	1.50	40	149(100), 167(31), 279(26)	149
benzo(a)anthracene	1.54	40	228(100), 229(19), 226(19)	228, 229, 257
benzo(b)fluoranthene	1.66	40	252(100), 253(23), 125(15)	252, 253, 281
benzo(k)fluoranthene	1.66	40	252(100), 253(23), 125(16)	252, 253, 281
benzo(a)pyrene	1.73	40	252(100), 253(23), 125(21)	252, 253, 281
indeno(1,2,3-cd)pyrene	2.07	100	276(100), 138(28), 277(27)	276, 277, 305
dibenzo(a,h)anthracene	2.12	100	278(100), 139(24), 279(24)	278, 279, 307
benzo(g h i)perylene	2.18	100	276(100), 138(37), 277(25)	276, 277, 305
N-nitrosodimethylamine			42(100), 74(88), 44(21)	
N-nitrosodi-n-propylamine			130(22), 42(64), 101(12)	
4-chloro-phenyl phenyl ether			204(100), 206(34), 141(29)	
endrin aldehyde				
3,3'-dichlorobenzidine			252(100), 254(66), 126(16)	
2,3,7,8-tetrachlorodibenzo-p-dioxin			322(100), 320(90), 59(95)	
bis(chloromethyl)ether			45(100), 49(14), 51(5)	
deuterated anthracene (d10)	1.09	40	188(100), 94(19), 80(18)	189, 217

1 1% SP-2250 on 100/120 mesh Supelcoport in a 6' x 2 mm id glass column; He @ 30 ml/min; Program: 50° for 4 min, then 8°/min to 260° and hold for 15 min.

* Conditioning of column with base is required.

Table III. Acid Extractables

Compound Name	RRT[1] (2-nitrophenol)	Limit of Detection (ng)	Characteristic EI ions (Rel. Int.)	CI ions (Methane)
-chlorophenol	0.63	100	128(100), 64(54), 130(31)	129, 131, 157
henol	0.66	100	94(100), 65(17), 66(19)	95, 123, 135
,4-dichlorophenol	0.96	100	162(100), 164(58), 98(61)	163, 165, 167
-nitrophenol	1.00	100	139(100), 65(35), 109(8)	140, 168, 122
-chloro-m-cresol	1.05	100	142(100), 107(80), 144(32)	143, 171, 183
,4,6-trichlorophenol	1.14	100	196(100), 198(92), 200(26)	197, 199, 201
,4-dimethylphenol	1.32	100	122(100), 107(90), 121(55)	123, 151, 163
,4-dinitrophenol	1.34	2 µg	184(100), 63(59), 154(53)	185, 213, 225
,6-dinitro-o-cresol	1.42	2 µg	198(100), 182(35), 77(28)	199, 227, 239
-nitrophenol	1.43	100	65(100), 139(45), 109(72)	140, 168, 122
entachlorophenol	1.64	100	266(100), 264(62), 268(63)	267, 265, 269
euterated anthracene (d10)	1.68	40	188(100), 94(19), 80(18)	189, 217

1 Column: 6' glass, 2 mm i.d.
Tenax GC - 60/80 mesh
180° - 300° @ 8°/min.
He @ 30 ml/min

Table IV. ELUTION ORDER OF MOST OF THE SEMIVOLATILE PRIORITY POLLUTANTS ON 1% SP2250[a]

Compound	RRT[b,c]
1,3-dichlorobenzene	0.35[d]
2-chlorophenol	0.35[e]
1,4-dichlorobenzene	0.36[d]
hexachloroethane	0.38
1,2-dichlorobenzene	0.39
bis(2-chloroisopropyl)ether	0.47
β-endosulfan	0.51
2,4-dimethyl phenol	0.52[e]
2-nitrophenol	0.53[e]
2,4-dichlorophenol	0.53[e]
hexachlorobutadiene	0.55
1,2,4-trichlorobenzene	0.55
naphthalene	0.57
bis(2-chloroethyl)ether	0.61
hexachlorocyclopentadiene	0.64
nitrobenzene	0.64
phenol	0.67
bis(2-chloroethoxy)methane	0.68
2,4,6-trichlorophenol	0.71[e]
p-chloro-m-cresol	0.73[f]
2-chloronaphthalene	0.76
acenaphthylene	0.83
acenaphthene	0.86
isophorone	0.87
fluorene	0.91

Table IV. ELUTION ORDER OF MOST OF THE SEMIVOLATILE PRIORITY POLLUTANTS ON 1% SP2250[a] (Continued)

Compound	RRT[b,c]
2,6-dinitrotoluene	0.93
1,2-diphenylhydrazine	0.96
2,4-dinitrotoluene	0.98
N-nitrosodiphenylamine	0.99
hexachlorobenzene	1.00
4-bromophenyl phenyl ether	1.01
α-BHC	1.02
γ-BHC	1.09[f]
phenanthrene	1.09[f]
anthracene	1.09
dimethyl phthalate	1.10
pentachlorophenol	1.11[f]
β-BHC	1.12
aldrin	1.14
diethyl phthalate	1.15
heptachlor	1.15
heptachlor epoxide	1.23
fluoranthene	1.23
α-endosulfan	1.24
dieldrin	1.28
4,4'-DDE	1.30
pyrene	1.30
di-n-butyl phthalate	1.31
4,4'-DDD (p,p'-TDE)	1.33
4,4'--DDT	1.38[d]
endosulfan sulfate	1.41[f]
endrin	1.41
benzidine	1.38
butyl benzyl phthalate	1.46
chrysene	1.46

Table IV. ELUTION ORDER OF MOST OF THE SEMIVOLATILE PRIORITY POLLUTANTS ON 1% SP2250[a] (Continued)

Compound	RRT[b,c]
bis(2-ethylhexyl)phthalate	1.50
benzo(a)anthracene	1.54
benzo(b)fluoranthene	1.66
benzo(k)fluoranthene	1.66
benzo(a)pyrene	1.73
indeno(1,2,3-cd)pyrene	2.07
dibenzo(a,h)anthracene	2.12[d]
benzo(ghi)perylene	2.12[f]

a 1% SP-2250 on 100/120 mesh Supelcoport in a 6' x 2mm id glass column; He @ 30ml/min; Program: 50° for 4 min, then 8°/min to 260° and hold for 15 min.

b Relative to hexachlorobenzene at 19.4 min.

c 40ng gives 5-90% response on FID unless otherwise noted.

d 200ng required to obtain 5-90% response on FID.

e 2 µg required.

f 40 µg required.

Table IV

(continued)

Standards not available: as of 2/8/77

N-nitrosodi-n-propylamine

4-chlorophenyl phenyl ether

TCDD

endrin aldehyde

N-nitrosodimethylamine

3,3'-dichlorobenzidine

bis(chloromethyl)ether (unstable in water)

Standards that would not chromatograph:

4,6-dinitro-o-cresol

4-nitrophenol

2,4-dinitrophenol

Standards yielding a range of peaks:

	RRT[b]
PCB-1242	0.93-1.24
PCB-1254	1.18-1.41
toxaphene	1.22-1.47
chlordane	1.14-1.37

Table V. Order of Elution for OV-17 SCOT Column[1]

Compound	Spectrum Number[2]
1,3-dichlorobenzene	134
1,4-dichlorobenzene	137
2-chlorophenol	141
1,2-dichlorobenzene	153
bis(2-chloroethyl)ether	163
phenol	165
bis(2-chloroisopropyl)ether	173
hexachloroethane	178
nitrobenzene	194
2-nitrophenol	219
1,2,4-trichlorobenzene	234
2,4-dimethylphenol	240
naphthalene	240
2,4-dichlorophenol	244
hexachlorobutadiene	262
isophorone	272
p-chloro-m-cresol	317
hexachlorocyclopentadiene	325
2,4,6-trichlorophenol	332
chloronaphthalene	339
2,4-dinitrotoluene	372
acenaphthylene	374
acenaphthene	390
dimethylphthalate	397
fluorene	434
diethylphthalate	447
N-nitrosodiphenylamine	447
2,6-dinitrotoluene	454
α-BHC	476
4-bromophenyl phenyl ether	478
γ-BHC	487
hexachlorobenzene	490
β-BHC	506
phenanthrene	518
anthracene	518
di-n-butylphthalate	583
aldrin	592
fluoranthene	617
pyrene	634
DDE	659
DDD	664
endrin	688
dieldrin	688
DDT	713
butyl benzyl phthalate	713
benzo(a)anthracene	748
chrysene	748

Table V. Continued

Compound	Spectrum Number[2]
bis(2-ethylhexyl)phthalate	804
benzo(a)pyrene	906
benzo(b)fluoranthene	970
benzo(k)fluoranthene	970

1 33 meter glass OV-17 SCOT column,
Program: 60° - 260° @ 6°/minute

2 Number of 2.5 second scans up to point of elution.

Metals

1. Sample Preparation

With the exception of mercury, the metals to be determined may be divided into two groups as follow:

a) those metals which are to be first analyzed by flame atomic absorption (AA), and, if not detected, then analyzed by flameless AA - Be, Cd, Cr, Cu, Ni, Pb and Zn,

b) those metals which are to be analyzed by flameless AA only - Ag, As, Sb, Se, and Tl.

For flame AA analysis the sample should be prepared using the procedure as given in "Methods for Chemical Analyses of Water and Wastes (1974)" 4.1.4 page 83. (See Appendix IV).

With the exception of antimony and beryllium, samples to be analyzed by flameless AA should be prepared as an industrial effluent as described in "Atomic Absorption Newsletter," 14, page 111 (1975). (See Appendix V) / Note: Nickel nitrate should be added only to those aliquots on which the analysis of selenium and arsenic are to be accomplished. The sample preparation procedure for antimony and beryllium analysis by flameless AA is the same procedure used for flame AA.

The sample preparation procedure to be used for mercury analysis is that given in "Methods for Chemical Analysis of Water and Wastes (1974)" 8.1 page 124. (See Appendix IV).

2. Apparatus

All samples are to be analyzed using an atomic absorption spectrophotometer equipped with simultaneous background capability. For arsenic, cadmium, antimony, selenium, thallium and zinc, either electrodeless discharge lamps or high intensity hollow cathode lamps may be utilized. A heated graphite atomizer is to be used for all flameless AA work. A strip chart recorder must be used as part of the readout system to detect and avoid the inclusion of extraneous data.

3. Procedure

a) Flame AA - The procedures to be used are those described in "Methods for Chemical Analysis of Water and Wastes (1974)" (see Appendix IV) as referenced in Table I below. Instructions as to when flameless AA is to be used are also included. For those instrumental parameters which are not defined in the recommended procedures, the instrument manufacturers recommendations are to be followed. Background correction is to be used on all analyses.

Table I

Element	Methods for Chemical Analysis of Water and Wastes, 1974*	Comments
Be	p. 99	Analyze by flameless AA if conc. <20 µg/
Cd	p. 101	Analyze by flameless AA if conc. <20 µg/
Cr	p. 105	Use nitrous oxide-acetylene flame for al analyses-analyze by flameless AA if conc. <20
Cu	p. 103	Analyze by flameless AA if conc. <50 µg/
Ni	p. 141	Analyze by flameless AA if conc. <100 µg
Pb	p. 112	Analyze by flameless AA if conc. <300 µg
Zn	p. 155	Analyze by flameless AA if conc. <20 µg/

*In those instances where more vigorous digestion for sample preparation is desired (or necessary) the procedure on page 82 (4.1.3) should be followed.

b) Standard solutions to be used for the flameless work should also be prepared as described in "Methods for Chemical Analysis of Water and Wastes (1974)". (See Appendix IV). The working standards should be diluted to contain the same acid concentration as the prepared samples. The instrumental settings and conditions recommended by the manufacturers are to be considered the procedural guidelines. In addition, the following requirements should also be incorporated into the procedure

1) Argon should be used as the purge gas in all analyses.
2) Background correction and method of standard addition must be used on all analyses.
3) A blank maximum temperature atomization, without gas interrupt, should be accomplished before each analytical determination.

4) The graphite tube or cuvette should be replaced as suggested by the instrument manufacturer or when contamination or lack of precision indicates that replacement is necessary.

5) All disposable pipet tips should be cleaned before use by soaking overnight in 5% redistilled nitric acid, rinsed with tap and deionized water, and dried.

6) The accuracy of the temperature indicator on the heated graphite atomizer should be verified before beginning any analytical work. This should be done by plotting charring temperature versus atomization signal and determining the maximum allowable charring temperature for a standard solution of a compound where the volatilization temperature is known. The compound used should have a volatilization temperature between 800 and 1200°C.

7) To insure that there is no loss from the acid matrix prior to atomization, the optimum charring temperature for each metal should be established in the same manner (i.e., by plotting charring temperature versus atomization signal of standard solution of each metal).

For the determination of selenium the procedure given for industrial effluents ("Atomic Absorption Newsletter," Vol. 14, page 109 [1975]) (see Appendix V) should be followed. Arsenic should be determined in the same manner (using the nickel nitrate matrix) with an optimum charring temperature of approximately 1300°C.

The analysis of zinc by flameless AA is difficult because of environmental contamination. The analyst must take precaution to provide a clean work area to minimize this problem.

c) Mercury analyses - The cold vapor technique as described in "Methods for Chemical Analysis of Water and Wastes, 1974" page 118 (Appendix IV) is to be followed.

6. Quality Assurance

a) To verify that the instrument is operating correctly within the expected performance limits, an appropriate standard should be included between every ten samples.

b) Spiked aliquots shall be analyzed with a frequency of 15% of the sample load for each metal determined by flame AA. If the recove is not within ±10% of the expected value the sample should be analyze by method of standard addition. (The spike should be added to the aliquot prior to sample preparation.) The amount added should increa the absorbance by not less than 0.01 units where the absorbance in the unspiked aliquot was less than 0.1, and not more than 0.1 when the absorbance in the unspiked aliquot was 0.1 or greater.

c) For mercury, the spike added should be an amount equal to five times the detection level.

Cyanides

3. Sample Preparation

All samples are to be distilled prior to determination for total cyanides. The distillation procedure given on page 43 of "Methods for Chemical Analysis of Water and Wastes, 1974" (see Appendix IV) is to be followed.

4. Sample Procedure

The procedure for total cyanides as given on pages 43-48 of "Methods for Chemical Analysis of Water and Wastes, 1974" (see Appendix IV) is to be followed.

5. Quality Assurance

a) Initially, determine 100% distillation efficiency on each distillation-digestion apparatus by comparing distilled standards to non distilled standards. Each day, distill at least one standard to confirm distillation efficiency and purity of reagents.

b) At least 15% of the cyanide analysis will consist of duplicate and spiked samples. Quality control limits are to be established and confirmed as described in Chapter 6 of the "Analytical Quality Control Handbook" (see Appendix VI).

6. Reporting of Data

Report cyanide concentrations as follows: less than 1.0 mg/l, nearest 0.01 mg; 1.0 mg/l and above, two significant figures.

PHENOLS

1. Sample Preparation

Distill all samples prior to determination of phenols. Use the procedure in "Standard Methods for the Examination of Water and Wastewater," 14th edition, 1975, p. 576 (Appendix X).

2. Procedure

Use method 510 for phenols in Appendix X, pages 577-580 and 580-581. Use method 510B for samples that contain less than 1 mg/l of phenol. Use method 510C for samples that contain more than 1 mg/l of phenol.

3. Quality Assurance

Determine that distillation efficiency is 100% on each distillatio apparatus by comparing distilled standards to non-distilled standards. Each day distill, at least, one standard to confirm the distillation efficiency and purity of reagents.

Run duplicate and dosed sample analyses on at least 15% of the samples analyzed for phenol. Establish and confirm quality control limits as described in Appendix VI.

4. Reporting of Data

Report phenol concentrations as follows:
Method 510B to the nearest µg/l.
Method 510C - when less than 1.0 µg/l to the nearest 0.01 mg; 1.0 mg/l and above to two significant figures.
Report all quality control data when reporting results of sample analysis.

List of Appendices (References)

I. Determining Volatile Organics at Microgram-per-Liter Levels by Gas Chromatography. T.A. Bellar and J.J. Lichtenberg, Jour. AWWA, p. 739-744, Dec. 1974.

II. Federal Register, Volume 38, number 125, part II, Appendix II, p. 17319, Friday, June 29, 1975, "Determination of Organochlori Pesticides in Industrial Effluents."

III. Reference Compound to Calibrate Ion Abundance Measurements in Gas Chromatography--Mass Spectrometry Systems. J.W. Eichelberg L.E. Harris and W.L. Budde, Anal. Chem. 47, 995-1000 (1975).

IV. Methods for Chemical Analysis of Water and Wastes (1974). U.S. Environmental Protection Agency, Technology Transfer.

V. Determining Selenium in Water, Wastewater, Sediment and Sludge by Flameless Atomic Absorption Spectroscopy. T.D. Martin and J.F. Kopp, Atomic Absorption Newsletter 14, 109-116 (1975).

VI. Handbook for Analytical Quality Control in Water and Wastewate Laboratories (1972). U.S. Environmental Protection Agency, Technology Transfer.

VII. ASTM Annual Standards - Water, part 31: (a) Method D2908 "Standard Recommended Practice for Measuring Water by Aqueous-Injection Gas Chromatography", (b) Method D3371 "Tentative Method of Test for Nitriles in Aqueous Solution by Gas Liquid Chromatograph", and (c) Harris, L.E., Budde, W.L., and Eichelberger, J.W., Anal. Chem., 46,1912 (1974), "Direct Analysis of Water Samples for Organic Pollutants with Gas Chromatography-Mass Spectrometry."

VIII. General Information

IX. Possible Sources for Some Priority Pollutant Standards.

X. "Standard Methods for the Examination of Water and Wastewater, 14 edition, 1975.

APPENDIX VIII

General Information

Emulsions

Limited work with several categories of industrial effluents covered by this study (tanneries, petroleum, soap and detergent, steam electric, pesticide) show that emulsions of widely differing frustration factors are often encountered in the extraction procedure. Samples that emulsify at basic pH usually also emulsify at acid pH. There are two equally acceptable alternatives available for the purposes of this protocol: break the emulsion or start over with fresh sample and use a continuous extractor, to prevent the formatio of emulsions.

By the 85% solvent recovery criteria, no way was found to break the emulsion formed on extraction of untreated tannery wastes. A soap and detergent sample was also very difficult. The use of a continuous heavier-than-water liquid extractor allowed the extractio to take place with no difficulties and very little labor. However, two days time is required. Comparison of samples from four industri petroleum, tannery, pesticide, and soap and detergent--by both shake and continuous extraction using wastes spiked with priority pollutan indicate that the two techniques are comparable. For some indiviual cases one technique is better than the other but no clear pattern emerges. Therefore, if desired, a continuous extraction technique may be used in place of separatory funnel extraction for all samples as well as those for which it is absolutely necessary because of intractable emulsions.

There is a justifiable concern that the extraction efficiency for these compounds may differ widely depending on the nature of the effluents. This is true but no better approach is apparent. For example, recoveries of most of the base-neutrals were judged to be about 75% from the tannery and petroleum samples but less than 25% from soap and detergent.

Appendix IX

Possible Sources for Some Priority Pollutant Standards

Compound	Source of Standard[2]
acenaphthene	AN p. 118
acrolein	AL p. 18
acrylonitrile	AL p. 19
aldrin	HERL #80
dieldrin	HERL #2380
benzene	B p. 154
benzidine[1]	ICN p. 27
carbon tetrachloride (tetrachloromethane)	B p. 88
chlordane (technical mixture & metabolites)	HERL #1200
Chlorinated benzenes (other than dichlorobenzenes)	
chlorobenzene	AL p. 165
1,2,4-trichlorobenzene	AL p. 710
hexachlorobenzene	AL p. 416
Chlorinated ethanes (including 1,2-dichloroethane, 1,1,1-trichloroethane and hexachloroethane)	
1,2-dichloroethane	AL p. 261
1,1,1-trichloroethane	B p. 309
hexachloroethane	AL p. 416
1,1-dichloroethane	PB p. 142
1,1,2-trichloroethane	PB p. 388
1,1,2,2-tetrachloroethane	PB p. 372
chloroethane	EA p. 53
Chloroalkyl ethers (chloromethyl, chloroethyl and mixed ethers)	
bis(chloromethyl) ether[1]	**
bis(2-chloroethyl) ether	AL p. 173
2-chloroethyl vinyl ether	AL p. 174
Chlorinated naphthalene	
2-chloronaphthalene	ICN p. 50

Possible Sources for Some Priority Pollutant Standards
(Continued)

Compound	Source of Standard[2]
Chlorinated phenols (other than those listed elsewhere; includes trichlorophenols and chlorinated cresols)	
2,4,6-trichlorophenol	AL p. 712
p-chloro-m-cresol	TCI p. 102
chloroform (trichloromethane)	B p. 92
2-chlorophenol	AL p. 187
DDT and metabolites	
4,4'-DDT	HERL #1920
4,4'-DDE	HERL #1860
4,4'-DDD (p,p'-TDE)	HERL #1780
Dichlorobenzenes (1,2-;1,3-; and 1,4-dichlorobenzenes)	
1,2-dichlorobenzene	AL p. 258
1,3-dichlorobenzene	AL p. 258
1,4-dichlorobenzene	AL p. 258
Dichlorobenzidine	
3,3'-dichlorobenzidine[1]	CPL p. 81
Dichloroethylenes (1,1-dichloroethylene and 1,2-dichloroethylene)	
1,1-dichloroethylene	AL p. 746
1,2-trans-dichloroethylene	AL p. 262
2,4-dichlorophenol	AL p. 265
Dichloropropane and dichloropropene	
1,2-dichloropropane	AL p. 267
1,3-dichloropropylene (1,3-dichloropropene)	AL p. 267
2,4-dimethylphenol	AL p. 323
Dinitrotoluene	
2,4-dinitrotoluene	PB p. 180
2,6-dinitrotoluene	PB p. 180
1,2-diphenylhydrazine	AL p. 338

Appendix IX

Possible Sources for Some Priority Pollutant Standards

(Continued)

Compound	Source of Standard[a]
Endosulfan and metabolites	
α-endosulfan	HERL #3220
β-endosulfan	HERL #3200
endosulfan sulfate	NI p. 45
Endrin and metabolites	
endrin	HERL #3260
endrin aldehyde	NI p. 147
ethylbenzene	B p. 161
fluoranthene	AN p. 118
Haloethers (other than those listed elsewhere)	
4-chlorophenyl phenyl ether (p-chlorodiphenyl ether)	RFR p. 6*
4-bromophenyl phenyl ether	ICN p. 37
bis(2-chloroisopropyl) ether	PB
bis(2-chloroethoxy) methane	PB p. 62
Halomethanes (other than those listed elsewhere)	
methylene chloride (dichloromethane)	PB p. 276
methyl chloride (chloromethane)	PB p. 277
methyl bormide (bromomethane)	PB p. 276
bromoform (tribromomethane)	PB p. 73
dichlorobromomethane	CO p. 16
trichlorofluoromethane	PB p. 358
dichlorodifluoromethane	PB p. 142
chlorodibromomethane	CO p. 27
Heptachlor and metabolites	
heptachlor	HERL #3860
heptachlor epoxide	HERL #3880
hexachlorobutadiene	AL p. 416
Hexachlorobyclohexane (all isomers)	
α-BHC	HERL #620
β-BHC	HERL #640
γ-BHC (lindane)	HERL #680
δ-BHC	HERL #660

Appendix IX

Possible Sources for Some Priority Pollutant Standards

(Continued)

Compound	Source of Standard[2]
hexachlorocyclopentadiene	AL p. 416
isophorone	AL p. 464
naphthalene	AN p. 118
nitrobenzene	AL p. 557
Nitrophenols (including 2,4-dinitrophenol and dinitrocresol)	
2-nitrophenol	AL p. 564
4-nitrophenol	AL p. 564
2,4-dinitrophenol	AL p. 332
4,6-dinitro-o-cresol	TCI p. 188
Nitrosamines	
N-nitrosodimethylamine[1]	NI p. 173
N-nitrosodi-n-propylamine	PB p. 310
N-nitrosodiphenylamine	EA p. 159
pentachlorophenol	AL p. 587
phenol	AL p. 595
Phthalate esters	
bis(2-ethylhexyl) phthalate	CS p. 8
butyl benzyl phthalate	CS p. 8
di-n-butyl phthalate	CS p. 8
diethyl phthalate	CS p. 8
dimethyl phthalate	CS p. 8
Polychlorinated biphenyls (PCB's)	
PCB-1242 (Arochlor 1242)	HERL #5703
PCB-1254 (Arochlor 1254)	HERL #5705
Polynuclear aromatic hydrocarbons (including benzanthracenes, benzopyrenes, benzofluoranthene, chrysenes, dibenzanthracenes, and indenopyrenes)	
1,2-benzanthracene	AN p. 118
benzo[a]pyrene (3,4-benzopyrene)	AN p. 118
3,4-benzofluoranthene	NI
11,12-benzofluoranthene	NI
chrysene	AN p. 118

Appendix IX

Possible Sources for Some Priority Pollutant Standards

(Continued)

Compound	Source of Standard[2]
acenaphthylene	AN p. 1
anthracene	AN p. 118
1,12-benzoperylene	AN p. 118
fluorene	AN p. 118
phenanthrene	AN p. 118
1,2:5,6-dibenzanthracene	AN p. 118
indeno (1,2,3-C,D)pyrene	AN p. 118
pyrene	AN p. 118
2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD)	NI p. 174
tetrachloroethylene	AL p. 680
toluene	AL p. 701
toxaphene	HERL #6740
trichloroethylene	AL p. 711
vinyl chloride (chloroethylene)	PB p. 406
1-bromodecane (possible internal standard)	
1-bromododecane (possible internal standard)	

Footnotes:

1 These compounds or any mixture containing 1% or more by weight of these compounds are defined as carcinogens in the Federal Register, Vol. 38, No. 144, pp. 20074-20076, 27 July 1973. Prescribed safety regulations for handling are in the Federal Register, Vol. 39, No. 20, pp. 3756-3797, 29 January 1974.

2 Only one source is listed even though several may be available. These sources are not to be interpreted as being endorsed by the EPA; they serve to show at least one vendor where each standard can be obtained. When several sources were available and compound purity was listed, the source having the highest purity material was selected.

* These compounds have been ordered but have not been received at Athens ERL as yet.

** No source has been found as yet.

Sources of Standards and Abbreviations

AL	Aldrich Chemical Co., Milwaukee, Wisc.; Catalog 1977-1978.
AN	Analabs, Inc., North Haven, Conn.; Catalog 18 (June 1976).
B	J. T. Baker Chemical Co., Phillipsburgh, N.J.; Catalog 750 (July 1975).
CS	Chem-Service, West Chester, Pa.; Bulletin CS-100-8 (1975).
CPL	Chemical Procurement Laboratories, College Point, N.Y.; 1975 catalog.
EA	Eastman Kodak Co., Rochester, N.Y.; Catalog 48 (1976).
ICN	K&K Rare & Fine Chemicals, Plainview, N.Y.; Catalog No. 10 (1975).
NI	Nanogens International, P.O. Box 487, Freedom, CA 95019 "Nanogen Index" (1975).
PB	Pfaltz & Bauer Chemical Co., STamford, Conn.; Catalog 1976.
RFR	RFR Corp., Hope, R.I.; "Chemical Standards for Air-Water-Industry-Foods" (1975).
HERL	"Analytical Reference Standards and Supplemental Data for Pesticides and Other Selected Organic Compounds", EPA-660/9-76-012 (May 1976), Health Effects Research Laboratory Environmental Toxicology Division, Research Triangle Park, NC. A sample order blank for standards and the above publication are attached.
CO	Columbia Organics Catalog A-7, Columbia, S.C. (1975).
TCI	Tridom Chemical Inc., Hauttauge, N.Y., Catalog No. 1 (1976).

ENVIRONMENTAL TOXICOLOGY DIVISION
HEALTH EFFECTS RESEARCH LABORATORY
UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
Research Triangle Park, North Carolina 27711

SUBJECT: Index of Pesticides Analytical Reference Standards - Update of Mailing List

DATE: June, 1976

FROM: Health Effects Research Laboratory, ETD, ACB, Research Triangle Park, NC, U.S.A. 27711 (MD-69)

J. F. Thompson

TO: All Laboratory Facilities on our Mailing List

This copy of the 1976 revision of our pesticides reference standards index was mailed to the address appearing on our mailing list. As this list is several years old, we are sure that a number of addresses have changed and that some are probably no longer existent.

If you wish to remain on our mailing list to receive future updates of this publication, would you be good enough to complete the mail-back below, snip it off, and return it to us. Do not tear off the back cover to return to the address shown. If you have no use for this publication but know of some other individual within your organization who is concerned with pesticides analysis, would you convey this index, along with the mailback, to that person.

To: U. S. Environmental Protection Agency
Health Effects Research Laboratory
Environmental Toxicology Division
Research Triangle Park, NC, U.S.A. 27711 (MD-69)

Date ________________

☐ We wish to be retained on your mailing list to receive future updates of the Pesticides Standards Index. The address shown on the envelope is entirely correct and requires no changes.

☐ We have no interest in future updates of this publication. Please cancel us from your mailing list.

☐ We wish to be retained on your mailing list, but the address shown on the envelope should be changed to read (print or type)

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Quality Assurance Section
Environmental Toxicology Division,
EPA, HERL, Research Triangle Park, NC 27711
MD-69

Date Request Recd	/ /
Shipment Date	/ /
Lab Code No.	
Order Filled by	
DO NOT WRITE IN THIS SPACE	

The following reference standards are required for our program:

Catalog Code No.	Compound (Catalog Name)	Catalog Code No.	Compound (Catalog Name)

If necessary, use back of sheet to complete list. Covering letter unnecessary if this form is completed in full.

Name and address of laboratory ____________________

Requestor's Name (Print or type)

IMPORTANT:

1. The amount of each standard is restricted to 100 mg because of the scarcity and expense of refining analytical grade materials.
2. Please return at once the acknowledgement card enclosed with each shipment. This provides the sole evidence of delivery of the shipment.
3. Do not request compounds not listed in the catalog. No others are stocked.
4. If a bottle appears to be empty, remove cap and examine interior of bottle and cap. Certain highly viscous materials tend to collect in cap.